

CHREV. 188

INORGANIC GAS CHROMATOGRAPHY

PETER C. UDEN

Department of Chemistry, University of Massachusetts, Amherst, MA 01003 (U.S.A.)

CONTENTS

1. Introduction	3
2. Gas chromatographic column materials	5
3. Gas chromatography of inorganic gases	6
4. Binary inorganic compounds	8
4.1. Inorganic halides	9
5. Thermochromatography	11
6. Organometallic compounds	11
6.1. Main group organometallics	11
6.1.1. Group II sigma-bonded compounds	11
6.1.1.1. Alkyl and aryl mercury compounds	11
6.1.2. Group III sigma-bonded compounds	12
6.1.2.1. Organoboron compounds	12
6.1.2.2. Organoaluminium and organogallium compounds	12
6.1.3. Group IV sigma-bonded compounds	13
6.1.3.1. Alkylgermanes and stannanes	14
6.1.3.2. Alkyllead compounds	14
6.1.4. Group V sigma-bonded compounds	15
6.1.5. Group VI sigma-bonded compounds	15
6.1.6. Alkylation and arylation reagents for inorganic elements	16
6.1.7. Metal and metalloid alkoxides and oxy-salts	16
6.2. Pi-bonded transition metal organometallics	16
6.2.1. Metal carbonyls and related compounds	17
6.2.2. Metallocenes and their derivatives	18
6.2.3. Metal chelates	18
6.2.3.1. Beta-diketones	19
6.2.3.2. Other beta-difunctional ligands	21
6.2.3.3. Dialkyldithiocarbamates	23
6.2.3.4. Dialkyldithiophosphinates	25
6.2.3.5. Metalloporphyrins	25
7. Emission spectroscopic detection in inorganic GC	26
7.1. The microwave induced helium plasma detector (MIP)	27
7.2. The d.c. argon plasma (DCP)	27
7.3. The inductively coupled argon plasma (ICP)	27
8. The past and the future of inorganic GC	27
References	28

1. INTRODUCTION

Since its inception more than 30 years ago, gas-liquid chromatography (GLC) has made the greatest impact on quantitative resolution of volatile organic compounds reinforced and extended by the growth of application of high resolution

capillary columns for separation of complex multicomponent samples Gas-solid adsorption chromatography (GSC) has its major application for light inorganic gas analysis but GLC and GSC analytical separation of metal complexes and organometallics has been less extensive than early expectations had suggested

There are a number of reasons for the relative sparcity of "inorganic" gas chromatographic analyses Inorganic compounds are often considered to be inherently non-volatilizable or thermally unstable under gas chromatographic conditions There is also considered to be inherent incompatibility of inorganic or organometallic compounds with column substrates and a prediction of undesirable reactivity making gas chromatography difficult if not impossible Some analytical chemists have been unwilling to explore inorganic gas chromatography because of assumed sample incompatibility with conventional detectors There are certainly instances where these drawbacks apply, but nonetheless there are many examples of valuable rigorous gas chromatography of metallic and metalloid compounds, this review considers such studies

In this review, the usual definitions of organometallics and metal complexes will be used The former will include compounds in which sigma or pi carbon to metal bonds are present Under the definition of metal complexes are compounds in which a coordinate bond is formed between a ligand atom such as oxygen, sulfur, nitrogen, phosphorus or halogen and a central metal atom The latter compounds comprise primarily metal chelate systems Many metallic compounds are excluded as they cannot be volatilized at conventional gas chromatographic column temperatures, however there are examples of successful elution of such compounds as metal oxides and halides at elevated temperatures The ionic form of many inorganic compounds as solid or in solution forbids direct gas chromatography but some times derivatization methods may enable successful elution to be achieved There are instances in which the great "reactivity" of metallic compounds is predicted to prohibit gas chromatography, but the non-oxidative and non-hydrolytic conditions of gas chromatography enable qualitative and quantitative separation to be carried out

A basic group of properties may be considered to be desirable for an "inorganic" compound before gas chromatography can be successful, these give a good guideline for experimental development They are "adequate" volatility, thermal stability, monomeric form, neutrality, relatively low molecular weight, coordinative saturation, and adequate structural shielding of the metal atom(s) by bulky and inert organic functional or coordinating groups The inorganic complex or organometallic compound should appear to the GC column as much like a simple organic compounds as possible and the "free" metal atom should never be exposed to reactive chromatographic substrates or materials The majority of successful quantitative GC separations of inorganic compounds follow most if not all of these criteria

The materials in the GC system are particularly important in defining the feasibility of inorganic gas chromatography The criteria of inert column materials, injection and detection pathways and ancillary flow devices is particularly important The advent of inert capillary column materials promises to reopen the study of many inorganic chromatographic applications

The development of novel detectors which are compatible, selective or specific for inorganic compounds has allowed quantitative and sensitive analysis that was unattainable earlier The time is ripe for the reappraisal of many of the early gas

chromatographic separations and analyses described in this review in the light of the advancing technology of the past few years and it is hoped that the discussion and appraisal of information will stimulate such studies

The methods of inorganic GC typically involve removal of interfering substances from those to be determined and increasing selectivity and sensitivity by sample treatment and preparation methods such as extraction and derivatization. The classes of inorganic materials for which GC is possible either directly or by indirect derivatization are

- (i) Elemental gases and vapors
- (ii) Binary inorganic compounds such as selected halides, hydrides and oxides
- (iii) Sigma-bonded organometallic and organometalloid compounds, *e.g.*, metal and metalloid alkyls and aryls
- (iv) Pi-bonded organometallics, *e.g.*, metal carbonyls and metallocenes
- (v) Chelated metal complexes having nitrogen, oxygen, sulfur, phosphorus etc as ligand atoms
- (vi) Derivatized species for metal, metalloid, non-metal or functional group determinations

2 GAS CHROMATOGRAPHIC COLUMN MATERIALS

While the first 25 years of GC may be considered as the age of packed column separations, the subsequent period has been characterized by rapid increase in open tubular capillary column emphasis. This trend which has culminated in the wide adoption of fused-silica open-tubular capillary columns has facilitated the highest resolution of multicomponent volatile mixtures in complex matrixes. Inorganic GC has not often had high resolution as its primary objective but has more usually aimed for the lowest detection limits for often intractable samples. Even so, there is a recent trend towards open-tubular column applications, this will undoubtedly revolutionize inorganic GC also.

Historically, inorganic GC separations have involved both adsorption and partition. The chemical reactivity of volatile inorganic compounds has frequently called for rigorous control of columns and substrates to prevent undesirable on-column decomposition or unfavorable interactions.

Adsorption GC has been mostly employed for the separation of gases, Kiselev and Yashin¹ reviewing applications to inorganic separations in their 1969 monograph. A wide variety of adsorptive column packings have been investigated, alumina, silica, other metal oxides, inorganic and carbon molecular sieves have been preferred for the separation of stable permanent atomic and molecular gases. Organic polymers, notably polystyrene copolymer based materials have been favored for more reactive and polar analytes such as hydrides, low-molecular-weight organometallics and polar compounds such as water and ammonia². Inorganic substrates such as quartz, diamond, metal salts and eutectics have been used for GC of reactive species at very high temperatures. The greater part of viable quantitative analysis has been by means of molecular sieves and porous polymers which show little residual adsorption.

The choice of partitioning stationary phases for separation of inorganic compounds has remained a challenge. With the exception of chromatography of particu-

larly stable compounds, polar substrates such as esters, polyesters and polyalkylene glycols such as CarbowaxesTM are not applicable. The main aim has been for analyte stability and the absence of on-column degradation rather than subtlety of resolution.

Methyl silicone oils and waxes have been most used although substituted silicones such as phenyl, cyano and particularly fluoroalkyl have also been favored. Elution problems and non-ideal chromatography have been frequent in inorganic GC and much effort has been expended to reduce them. Column materials, solid supports, treatment and deactivation, injection port design and system pre-treatment have all been considered. Most work has been with glass or stainless-steel columns, the former being usually preferred. Since metals deposited on internal column surfaces or supports can cause catalytic decomposition, there is always danger of increased sample degradation as more metals and oxides are deposited.

The adoption of capillary column techniques suggests as much advance for inorganic separations from the absence of decomposition sites on supports or columns, as by high resolution capabilities. This is particularly the case for fused-silica capillary columns which have extremely low trace metal levels in the silica matrix. It is probable that the many packed column partition or adsorption separations and stainless-steel or glass capillary GC described in this review will benefit from reassessment on fused-silica columns where thermal stability will prove to be the most important criterion for successful quantitative elution.

3 GAS CHROMATOGRAPHY OF INORGANIC GASES

Although published in 1973, *Gas Chromatography in Inorganics and Organometallics* by Guiochon and Pommier³ provides an excellent summary of this topic. It may be augmented by Schwedt's coverage in *Chromatographic Methods in Inorganic Analysis*⁴. Gas-liquid partition chromatography has limited applicability for permanent gases as partitioning into liquid phases is minimal at ambient or subambient temperatures. This, and their low boiling points minimized selectivity and retention. Although there have been reports of GLC of polar gases such as ammonia with ester and silicone oil phases, gas-solid adsorption is the preferred method for both polar and non-polar atmospheric gases. Zeolite-based molecular sieves with concentrated surface charge generate surface adsorption based on polarizability of adsorbed molecules⁵, these have been widely used for atmospheric gases.

Among the many examples that could be cited in this area, the study of Aubeau *et al*⁶ is noteworthy, they investigated the effect of the hydration level of a 5 Å molecular sieve on the separation and elution order of nitrogen, oxygen, hydrogen, methane, krypton, xenon and carbon monoxide. At 9.37% hydration the sequence of elution was H₂, N₂ + O₂, CO, CH₄ + Kr and Xe, however, at 1.53% hydration the order was H₂, O₂, N₂ + Kr, CH₄, CO and Ze. Reproducible hydration proves of the greatest importance in these analyses.

Although not widely applied, capillary columns for GSC having adsorbent coated as small particles on the inner column walls (the SCOT —support-coated open-tubular column) are of interest⁷.

The situation in which carbon dioxide is also present in gas mixtures is complicated since it is irreversibly retained by molecular sieves under normal conditions. Silica however, will permit resolution of all light gases except oxygen and nitrogen,

TABLE 1

SEPARATION MATERIALS FOR ADSORPTION GAS CHROMATOGRAPHY OF INORGANIC SUBSTANCES

Material condensed from ref 4, p 43

<i>Separation material</i>	<i>Typical separations</i>	<i>Ref</i>
Alumina	O ₂ , N ₂ , CO ₂	12
Beryllium oxide	H ₂ S, H ₂ O, NH ₃	13
Silica gel	O ₂ /N ₂ , CO ₂ , O ₃ , H ₂ S, SO ₂	14-16
Chromium(III) oxide	O ₂ , N ₂ , Ar, He	17
Clay minerals (Attapulgite, Sepiolite)	O ₂ , N ₂ , CO, CO ₂	18
Kaolin	He, O ₂ , N ₂ , CO, CO ₂	19
Sodium, lithium fluoride, alumina	MoF ₆ , SbF ₅ , UF ₆ , F	20
Quartz granules	Ta, Re, Ru, Os, Ir oxides, hydroxides	21
Chromosorb 102	Element hydrides	22
Graphite	NH ₃ , N ₂ , H ₂	23
Synthetic diamond	CF ₂ O, CO ₂	24
Molecular sieve	Hydrogen isotopes	25
Carbon molecular sieve	O ₂ , N ₂ , CO, CO ₂ , N ₂ O, SO ₂ , H ₂ S	26
XAD resins	NH ₃ , SO ₂ , H ₂ S, CO, CO ₂ , H ₂ O	27
Porapak Q	GeH ₄ , SnH ₄ , AsH ₃ , SbH ₃ , Sn(CH ₃) ₄	28,30
Porapak QS polymers	H ₂ S, CH ₃ SH, (CH ₃) ₂ S, (CH ₃) ₂ S _x , SO ₂	29
Porapak P	Chlorides of Si, Sn, Ge, P, As, Ti, V, Sb	31
Teflon	F, MoF ₆ , SbF ₆ , SbF ₃	32

and complete resolution is obtained by placing silica and molecular sieve columns in series separated by a low-volume non-destructive detector. Silica is widely used for separation of sulfur gases such as COS, H₂S, CS₂ and SO₂ (ref 8)

Water is often a chromatographic problem since adsorptive tailing is seen with most substrates. Porous polystyrene or related polymers such as Porapak™ and Chromosorb Century™ (refs 9 and 10) have very low affinity for water and this is

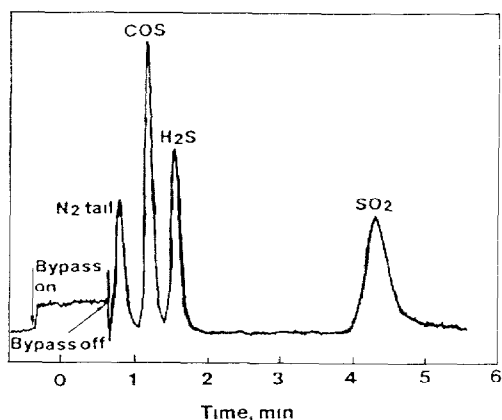


Fig 1 Chromatogram of 5 ppm each of COS, H₂S and SO₂ in N₂ Sample, 1 ml, column, 6 ft × 1/8 in O D Teflon packed with Chromosil 310, temperature, 60°C, flow-rate, 15 ml/min He, total flow to plasma, 60 ml/min He, forward microwave power, 100 W, reflected power, 4 W, sulfur emission line, 182.04 nm (From ref 33)

eluted rapidly with good peak shape as are polar compounds such as ammonia, hydrogen cyanide and sulfur dioxide. These polymers are also used in series with molecular sieves or as column pairs at different temperatures. Two Porapak QTM columns in series at 75°C and -65°C gave full resolution of CO₂, H₂S, H₂O, COS, SO₂, N₂, O₂, Ar and CO, helium carrier gas with 100 ppm of SO₂ added being used¹¹. A summary of adsorption materials and applications is given in Table 1.

Detection for inorganic gas analysis has been mainly by thermal conductivity since ionization detector response is very low. The prospect for enhanced detection by specific element methods involving atomic plasma emission spectroscopy is an attractive one since elemental response is independent of molecular form.

Genna *et al*³³ have shown the usefulness of the atmospheric pressure microwave-induced helium plasma (MIP) for specific element spectral emission detection of sulfur gases. Fig. 1 shows such a separation of COS, H₂S and SO₂ at the low ppm level. Detection limits for 1-ml sample volumes were 50, 100 and 100 ppb respectively.

4 BINARY INORGANIC COMPOUNDS

The main group hydrides and some halides have adequate vapor pressures and thermal stabilities at normal gas chromatographic temperatures and if column temperatures of 1000°C or higher are included, some metal oxides may also be eluted unchanged.

Among inorganic hydrides, those of Group IIIA, IVA and VA elements are viable for GC. Boron hydrides were among the earliest inorganic compounds gas chromatographed, silicon, germanium and tin hydrides have been widely studied, and selenium, tellurium, arsenic, antimony, bismuth and phosphorus have also been investigated. Boiling points range from -112°C for SiH₄ to -2.2°C for TeH₂.

An early hydride separation was of the borane homologues from diborane to pentaborane³⁴, low column temperatures and an inert system minimizing on-column degradation. Sowinski and Suffet^{35,36} obtained successful boron hydride separations with programmed-temperature GC. The reactivity of aluminium, gallium and indium hydrides indicates sub-ambient capillary GC to be the likely approach to their separation. These and similar separation methods are attracting renewed attention in view of the need for trace level determinations in electronic grade organometallics.

Silicon and germanium hydrides were also analyzed in early GC studies. Timms *et al*³⁷ separated silanes with up to eight silicon atoms and Feher and Strock³⁸ chromatographed compounds as high as Si₁₈H₁₈. Pollard *et al*³⁹ employed gas density detection for alkyltin mono- and dihydrides, inert stationary phases being needed to avoid on-column reaction.

Soderquist and Crosby⁴⁰ developed a comprehensive method for the simultaneous determination of triphenyltin hydroxide and its potential degradation products tetraphenyltin, diphenyltin oxide, benzene stannic acid and inorganic tin. The organotin compounds were converted to phenyltin hydrides by lithium aluminium hydride, separated and detected by electron capture. Minimum detectable quantities for Ph₃SnH, Ph₂SnH₂ and PhSnH₃ were *ca* 200 pg.

Zorin *et al*⁴¹ resolved arsine, phosphine, silane, and germane on a packed column of silicone oil coated on alumina at 30°C. Arsine was decomposed to hydrogen at 1000°C before thermal conductivity detection. More recently, arsine, stibine,

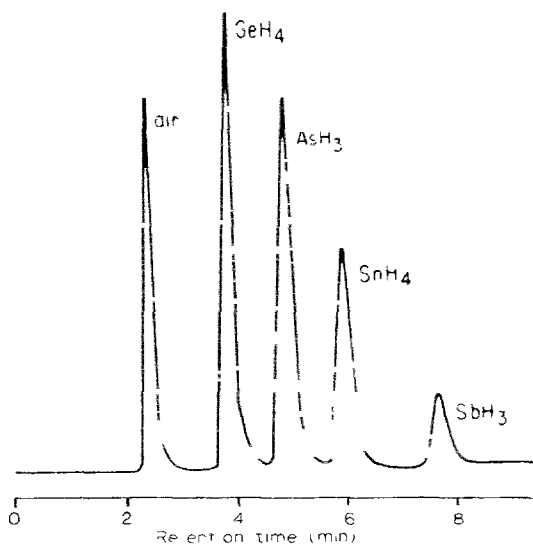


Fig 2 Separation of metalloid hydrides Column, 3 ft Porapak Q, temperature program, from 75 to 120°C at 8°C min (From ref 42)

germane and stannane were resolved in a porous polymer packed column by Kadeg and Christian⁴² (Fig 2) This study involved hydride generation with trapping of analytes prior to GC, atomic absorption spectroscopy detection was used Dumas and Bond⁴³ measured 0.01 ppm of phosphine after absorption on TenaxTM or Chromosorb 102

Caruso and co-workers used interfaced atomic absorption spectrophotometry⁴⁴ and MIP⁴⁵ detection for specific element monitoring of arsine, stibine, germane, stannane and hydrogen selenide on Chromosorb 102 columns Gifford and Bruckenstein⁴⁶ used a gas porous gold electrode for electrochemical detection of arsenic, antimony, tin and mercury hydrides GC of environmentally significant arsenic and antimony compounds with MIP detection was achieved by Talmi and co-workers^{47, 48}, who reduced alkylarsonic acids to alkylarsines with sodium borohydride prior to GC separation

4.1 Inorganic halides

A second major group of binary metal and metalloid compounds gas chromatographed at normal temperatures are the halides, but difficulties often lie in their high reactivity in vapor and condensed phases Inert chromatographic systems and care in sample handling are vital Among chlorides gas chromatographed are those of titanium, aluminium, mercury tin, antimony, germanium, gallium, vanadium, silicon, arsenic and phosphorus, all of which are readily hydrolyzed, particularly at elevated temperatures Elution problems may arise from reaction with even unreactive stationary phases such as methyl silicone oils, Sie *et al*⁴⁹ used inert fluorocarbon packings for reactive chlorides and oxychlorides including VOCl_3 , VCl_4 , PCl_3 and AsCl_3 Parissakis *et al*³¹ applied the porous polymer stationary phase Porapak PTM

for silicon, tin, germanium, vanadium, arsenic, antimony, titanium and phosphorus chlorides. Low melting inorganic salts, eutectics and metal phases have been used with considerable success, thus, Juvet and Wach⁵⁰ separated $TiCl_4$ and $SbCl_3$ on a $BiCl_3$ - $PbCl_2$ eutectic at $240^\circ C$ and Pommier *et al*⁵¹ reported the separation of $NbCl_5$ and $TaCl_5$ at $444^\circ C$ on a $LiCl$ - KCl eutectic. Tohyama and Otazai⁵² made an extensive study of eutectic and single chloride phases from 450 to $1000^\circ C$ using electrical conductivity detection. A recent application has involved determination of traces of plutonium in soil⁵³ which was decomposed by hydrofluoric acid and the residue chlorinated to either $PuCl_3$ or $PuCl_4$, alpha spectroscopic detection was used. The mechanism of separation operating in these cases may involve the formation of chloro complexes with free chloride ions present in the liquid phase.

The volatile silicon tetrahalides of chlorine and bromine are effectively separated on silicone oils coated on a polytetrafluoroethylene support⁵⁴ using hydrogen carrier gas. Crompton⁵⁵ provides a comprehensive survey of chlorosilane separations. The less volatile inorganic bromides are more difficult to chromatograph, high temperature stationary phases being usually necessary. Tsalas and Bachmann⁵⁶ used alkali bromide salts coated on silica as stationary phases. Bromine-nitrogen and boron tribromide-bromine-nitrogen mobile phases enabled quantitative elution of zinc, niobium, molybdenum, technetium, indium, antimony, tin, bismuth, tellurium and iodine bromides. Detection was by gamma ray spectroscopy of radiochemically labelled eluates. Although they could not all be fully resolved in one chromatogram, separations were possible by varying elution parameters. A typical chromatogram is shown in Fig. 3.

By contrast, many metal fluorides have low boiling points, *e.g.*, tungsten ($17.5^\circ C$), molybdenum ($35^\circ C$), tellurium ($35.5^\circ C$), rhenium ($47.6^\circ C$) and uranium

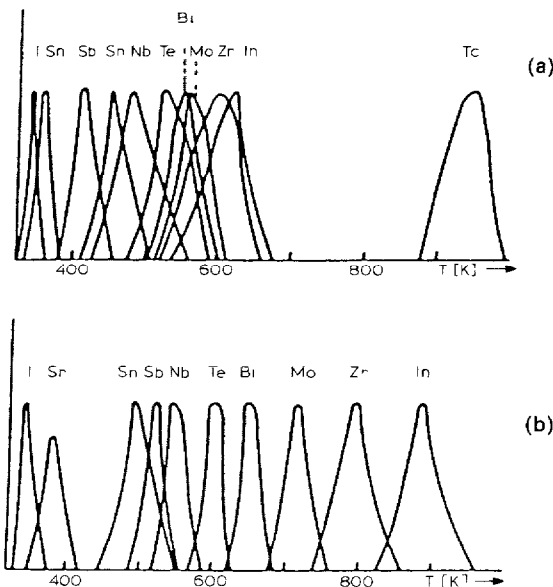


Fig. 3 Separation of inorganic bromides. Carrier gas, 60 mmHg of Br_2 and 4 mmHg of BBr_3 in N_2 . Stationary phases (a) $NaBr$, (b) KBr on quartz granules. Temperature program, 400 - $900^\circ C$ (From ref 56)

(56 2°C) Juvet and Fisher⁵⁷ obtained good peak shapes and separation at 75°C on a column of Kel-F oilTM coated on Chromosorb TTM (TeflonTM) Total absence of water was vital to preserve columns, detectors and other equipment The determination of alloys and metal oxides, carbides etc after conversion to fluorides by fluorination appears feasible

5 THERMOCHROMATOGRAPHY

Among extreme modifications of conventional gas chromatography is "thermochromatography" —very high temperature GC The applications for chlorides and particularly bromides were mentioned above but the most striking examples are of metal oxides, hydroxides and oxychlorides Steffen and Bachmann⁵⁸ have pioneered this demanding research area and have employed temperatures up to 1500°C to separate oxides and hydroxides of technetium, rhenium, osmium and iridium Quartz granules were used as substrate and oxygen and oxygen-water mixtures as carrier gases The mechanisms for these separations are uncertain since a differential volatilization-distillation process may apply rather than adsorption or partition As carefully designed instrumentation is needed it is likely that their utility will remain in physicochemical and not in analytical applications

6 ORGANOMETALLIC COMPOUNDS

In the introduction to his 1981 text *Gas Chromatography of Organometallic Compounds*⁵⁵, Crompton notes that during the preceding decade over 1000 papers appeared on this area, covering compounds of over 50 elements Organometallic compounds contain at least one metal to carbon bond, other than as found in metal carbides, metal carbonyls and their derivative compounds are also included Metal complexes chelated with ligands through oxygen, nitrogen, sulfur or phosphorus donor atoms are considered separately Organometallics may be classified according to the ligand type, period metal group or bonding type(s) A useful classification for gas chromatography is as "main group" organometallics with "sigma" carbon-metal bonds and as "transition group" compounds with pi carbon-metal bonding

6.1 Main group organometallics

Organometallics which have been gas chromatographed or for which GC is possible are Hg from Group II, B, Al, Ga and In from Group III, Si, Ge, Sn and Pb from Group IV, As, Sb and Bi from Group V and Se and Te from Group VI Silicon, lead, tin, arsenic and mercury compounds have been most investigated

The bonded organic functionalities are alkyl, aryl and substituted aryl groups, perfluoroalkyl and aryl groups and mixed alkyl-chloro and aryl-chloro systems Alkoxy groups also are common for silicon and in this group may be placed siloxanes, stannoxanes and carboranes

6.1.1 Group II sigma-bonded compounds

6.1.1.1 Alkyl and aryl mercury compounds The GC of these environmentally important compounds has attracted considerable attention, biomethylation of inorganic mercury being a significant natural process

Packed column GC was used by Baughman *et al*⁵⁹ for methylmercurials and phenylmercurials $(\text{CH}_3)_2\text{Hg}$ and $(\text{C}_6\text{H}_5)_2\text{Hg}$ were stable but some decomposition of organomercury halides was shown. Bache and Lisk⁶⁰ measured $(\text{CH}_3)_2\text{Hg}$ and CH_3HgCl with MIP detection. Risby and Talmi⁶¹ note in their review of MIP GC detectors that a GC-MIP system has long been in regular use in routine determination of methylmercurials⁴⁸ at sub-pg detection limits.

Non-flame "cold vapor" atomic absorption spectrophotometry at 254 nm has proved useful. Longbottom⁶² reduced organomercurials to elemental mercury over Cu_2O at 800°C , detection limits of 20 pg were obtained for dimethyl, dipropyl and dibutylmercury. Another spectroscopic detector found effective for organomercurials was the atmospheric pressure active nitrogen afterglow system (APAN) of Rice *et al*⁶³, a detection limit for dimethylmercury of 2 pg being reported.

Shaviat⁶⁴ converted dialkylmercurials to alkylmercuryiodides to exploit the sensitivity of the electron-capture detector.

Procedures for determination of environmental organomercurials are well reviewed by Crompton⁵⁵. Diphenylmercury and phenylmercury halides have been quantitatively determined, quantitative conversion of phenylmercuric nitrate to the chloride being applied for trace chloride measurement⁶⁵.

6 1 2 Group III sigma-bonded compounds

6 1 2 1 *Organoboron compounds* Although considerably more reactive than some metalloids, alkylboranes were investigated early by GC. Schomberg *et al*⁶⁶ studied alkyl group redistribution reactions between triethyl, tri-*n*-propyl and tri-isobutyl boranes, and Koster and Bruno⁶⁷ considered alkyl interchange among trialkylboranes and the analogous organoaluminum compounds. Higher alkylborane homologues up to decaboranes have been examined⁶⁸. It is probable that modern inert capillary columns may stimulate renewed study of these compounds.

An important group of compounds for gas chromatography is the DextsilTM range of carborane-silicone polymers whose high temperature stability has made them useful as stationary phases up to 400°C and above. The GC behavior and heats of solution in various stationary phases have been measured for carborane monomers of different structure⁶⁹.

6 1 2 2 *Organoaluminum and organogallium compounds* The thermal and chemical stability of the alkyl and other carbon bonded derivatives of Group III elements decreases with increasing atomic number and little GC has been reported. However, interest in their chemistry is increasing from applications as polymerization catalysts (aluminum alkyls) and electronic material precursors (gallium and indium alkyls).

The two reported separations of aluminum alkyls involve different approaches. Bortnikov *et al*⁷⁰ used a packed methyl silicone column at 110°C and thermal conductivity detection, but it was not clear whether any decomposition occurred. Longi and Mazzochi⁷¹ used a column outlet pressure of 350 torr to decrease decomposition during elution. Triethylaluminum was claimed eluted but there was extensive peak tailing. Specific element monitoring of eluate would be valuable in further such investigations. Trimethylgallium was also reported by Bortnikov *et al*⁷⁰ and by Fukin *et al*⁷² who identified $(\text{CH}_3)_2\text{GaCl}$, CH_3GaCl_2 and $(\text{CH}_3)_2\text{AlCl}$ by means of post-column analysis.

6.1.3 Group IV sigma-bonded compounds

The most extensive gas chromatography of sigma-bonded inorganics has been for Group IVA compounds. The very extensive application of GC in organosilicon chemistry is emphasized by Crompton who devotes more than 160 pages in his text⁵⁵ to alkyl and aryl silane and siloxane separation. Tetraalkylsilanes have often been chromatographed, their elution behavior paralleling alkanes. Logarithmic retention plots are linear with respect to parameters such as boiling point and molecular weight. Retention linearity was noted for tetraalkylsilanes from tetramethyl (C_4) to tetra(*n*-octyl) (C_{32})⁷³. Fig. 4 shows a capillary separation of a redistributed tetraalkyl silane mixture of 35 compounds formed by a catalyzed reaction of methylethyl-*n*-propyl-*n*-butylsilane⁷⁴. Dual detection is by a flame ionization (FID) and a microwave induced and sustained helium plasma (MIP) monitoring at 251.6 nm for silicon. Statistical alkyl group interchange predicts peak area ratios of 12, 24, 12, 12, 4 and 1 for $CH_3C_2H_5Si(n-C_3H_7)_2$, $CH_3C_2H_5Si-n-C_3H_7-n-C_4H_9$, $CH_3C_2H_5Si(n-C_4H_9)_2$, $C_2H_5-n-C_3H_7Si(n-C_4H_9)_2$, $n-C_3H_7Si(n-C_4H_9)_3$ and $Si(n-C_4H_9)_4$, these ratios are well shown in the chromatogram.

The great importance of methylchlorosilanes in silicone production ensured that their qualitative and quantitative separation was thoroughly investigated despite

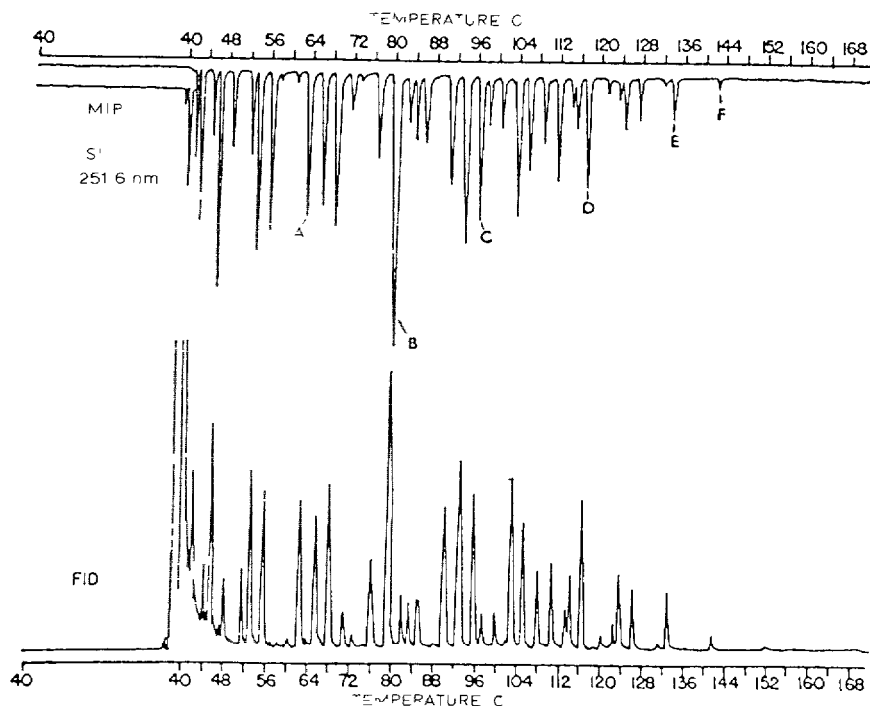


Fig. 4 Dual-detection chromatogram of the redistribution products of methylethyl-*n*-propyl-*n*-butylsilane. Column, 100 m \times 0.25 mm I.D. OV 225 glass capillary support-coated open tubular column. Temperature program, 40–170°C at 4°C/min. Lower chromatogram, FID, upper chromatogram MIP for silicon at 251.6 nm. Peak identities, A = methylethyl-di-*n*-propylsilane, B = methylethyl-*n*-propyl-*n*-butylsilane, C = methylethyl-di-*n*-butylsilane, D = ethyl-*n*-propyl-di-*n*-butylsilane, E = propyltri-*n*-butylsilane, F = tetra-*n*-butylsilane (From ref. 74).

their facile hydrolysis Burson and Kenner⁷⁵ obtained quantitation for methylchlorosilanes at the 100-ppm level in silicon tetrachloride and trichlorosilane, and GC of phenylchlorosilanes has been successfully accomplished at column temperatures above 200°C⁷³ Wurst and Churacek⁷⁶ gave retention data for alkyl and arylchlorosilanes, vinyl chlorosilanes and substituted siloxanes

6 1 3 1 Alkylgermanes and stannanes The GC of alkyl germanium and tin compounds is similar to that of silicon analogs although there is some tendency towards decreasing thermal stability, and Pollard *et al*⁷⁷ chromatographed alkylgermanes deriving from *n*-alkyl redistribution of groups up to *n*-butyl Bortnikov *et al*⁷⁸ separated germanium compounds with bonds between germanium, tin, silicon and sulfur heteroatoms by GLC and GSC The properties of alkylstannanes resemble the germanes except that more care is needed to prevent on-column oxidation, hydrolysis or thermal degradation Pollard *et al*.^{39,79} studied alkyl-, vinyl- and arylstannanes extensively, a gas density balance detector being used for $(\text{CH}_3)_3\text{SnH}$, $(\text{CH}_3)_4\text{Sn}$ and $(n\text{-C}_3\text{H}_7)_2\text{SnH}_2$ ³⁹ Redistribution reactions of substituents on tin and among adjacent Group IVA elements have been investigated with plasma emission specific element detection^{74,77}

Selective detection has been often used successfully for organotin compounds Flinn and Aue⁸⁰ used flame photometric detection (FPD) and gas phase luminescence, the response factor found for tin and germanium being six orders of magnitude greater than for hydrocarbons Kapila and Vogt⁸¹ also studied tetraalkylstannanes with FPD, monitoring in blue and red spectral regions Best results were with a 610-nm optical filter Hansen *et al*⁸² have used hydrogen atmosphere flame ionization detection (HAFID) for selective determination of metal compounds HAFID has selectivity three or more orders of magnitude over carbon while retaining normal sensitivity Applications of this system included bis(tributyltin)oxide (TBTO) in marine paints, triphenylhydroxystannane pesticide by derivatization to triphenylmethylstannane and tricyclohexylhydroxystannane (PlictanTM) in apple leaves by derivatization to tricyclohexylbromostannane Another interesting application of tetraalkyltin chemistry in GC was that of Rodriguez-Vazquez⁸³ who derivatized mercury to methylmercuric chloride with tetramethylstannane before GC

6 1 3 2 Alkyllead compounds The GC of the environmentally significant tetraalkyllead compounds is extensive They are generally more toxic than inorganic lead compounds, the toxicity varying with the extent of alkylation, the question of bioalkylation of inorganic to organic lead by microorganisms remaining debatable^{84,85} Selective detectors have been particularly widely applied for these compounds

HAFID has been used successfully for specific lead detection^{86,87} with detection limits of $7.2 \cdot 10^{-12}$ g/sec of lead in a method which simply employed a 1 10 dilution of leaded gasoline

Atomic spectroscopy has been quite extensively used for lead specific detection. Mutsaers and Van Steen⁸⁸ used FPD detection with an oxygen-hydrogen flame at 405.8 nm Atomic absorption spectroscopy (AAS) has had wide favor, flame atomic absorption being used by Ballinger and Whittemore⁸⁹ at 283.3 nm to give a 20-ng detection limit for lead Chau and co-workers^{90,91} carried out GC-AAS studies on quantitation of mixed methylethylleads in water sediment and fish samples to investigate bioalkylation, typical lead detection limits were from 0.01 to 0.025 $\mu\text{g/g}$ for

solid samples Radzuik *et al*⁹² also used GC-AAS for alkylleads in air, with better detection results by graphite furnace (GF) electrothermal atomization at 1500°C, sampling 70 liter air volumes condensed at -72°C Total alkyllead concentrations were found at 70 ng per cubic meter of air Robinson *et al*⁹³ also used GC-GFAAS with direct interfacing of the column into the furnace atomizer and these methods appear well established

With the increasing interest in plasma atomic emission detection, applications for alkylleads are of note The primary plasma employed has been the microwave induced and sustained helium plasma (MIP), early applications focusing on reduced pressure plasmas, Reamer *et al*⁹⁴ reporting a 3/4 wave Evensen cavity for atmospheric alkyllead determinations Air sampling was carried out and levels of tetramethyllead determined from 7 to 650 ng/m³ The atmospheric pressure microwave cavity of Beenakker⁹⁵ permits direct GC interfacing Qumby *et al*⁹⁶ obtained a detection limit of 0.49 pg/sec of lead in tetraethyllead, measured at 283.3 nm Its selectivity was seen in determination of mixed alkylleads in gasolines⁹⁷, a detection limit of 0.17 pg/sec and a selectivity over carbon of 246,000 being noted

The high toxicity of tetraalkylleads derives from their ability to undergo this decomposition $R_4Pb \rightarrow R_3Pb^+ \rightarrow R_2Pb^{2+} \rightarrow Pb^{2+}$ The formation in tissues of alkyllead salts such as chlorides, carbonates or nitrates, from rapid metabolic dealkylation of tetraalkylleads is of toxicological importance The GC of trialkyllead as the chloride is difficult but Estes *et al*⁹⁸ devised an inert capillary GC system of a fused-silica silicone oil column and a deactivated quartz interface to the MIP detector Trimethyl- and triethyllead chlorides were determined in water between 10 ppb and 10 ppm An alternative approach⁹⁹ derivatized trialkyllead by a butyl Grignard reagent to produce trialkylbutylleads A pre-column TenaxTM trap concentration enabled low-ppb determinations of the trialkyllead

6.1.4 Group V sigma-bonded compounds

The alkyl and aryl derivatives of arsenic and antimony are less stable than those of group IV elements and present more of a GC challenge Gudzinowicz and Martin¹⁰⁰ chromatographed methyl-, ethyl- and butylbromoarsines, trimethyl-, triphenyl- and trivinylarsine but a 290°C column temperature was needed for phenyl derivatives Parris *et al*¹⁰¹ used GC-GFAAS to measure trimethylarsine in micro-biologically generated gases using a packed silicone column at 40°C Schwedt and Ruessel¹⁰² determined 2 ppm of arsenic in biological materials by derivatization to triphenylarsene Sigma-bonded organoarsenicals may be quite readily eluted on fused-silica capillary columns Although much less GC is recorded for organoantimony compounds, the good peak characteristics of triethylantimony⁷¹ suggest alkylantimony compounds as suitable to quantitative separation Talmi and Norvell⁴⁸ determined environmental As³⁺ and Sb³⁺ by co-crystallization with alpha-mercapto-N,2-naphthylacetamide followed by reaction with phenylmagnesium bromide to triphenylarsine and triphenylstibine GC detection was by low pressure microwave plasma at 228.8 nm and 259.8 nm respectively with detection limits of 20 pg and 50 pg Alkylarsenic acids in pesticides and environmental samples were determined as alkylarsines generated by sodium borohydride reduction⁴⁷

6.1.5 Group VI sigma-bonded compounds

The chromatography of dialkylselenides and dialkyldiselenides was studied by

Evans and Johnson¹⁰³, the latter gave high response by electron-capture detection up to $1.5 \cdot 10^4$ times higher than the former Parris *et al*¹⁰¹ used GC-GFAAS for dimethylselenide as did Talmi and Audsen¹⁰⁴ and Estes *et al*¹⁰⁵ who obtained detection for selenium at 62 pg/sec

6.1.6 Alkylation and arylation reagents for inorganic elements

A range of reagents and substrates have been used to generate volatile alkyl and aryl metal or metalloid derivatives suitable for GC determination. A version of the summary by Schwedt⁴ is seen in Table 2.

6.1.7 Metal and metalloid alkoxides and oxy-salts

Many alkoxides share GC characteristics with organometallic alkyl compounds. The group IV elements silicon, germanium, tin, titanium, zirconium and hafnium form stable volatile alkoxides as do some Group III elements, particularly aluminum. Brown and Mazdiyasn¹¹³ separated isopropyl and *tert*-pentyl alkoxides on Teflon™ supports lightly loaded with Apiezon or silicone oil. Care was necessary to minimize exposure to moisture, mass and infrared spectroscopy confirmed elution of the eluted compounds undecomposed.

Separations were obtained for oxycarboxylate salts of beryllium and zinc. Barratt *et al*¹¹⁴ showed that beryllium oxyacetate, $\text{Be}_4\text{O}(\text{COOCH}_3)_6$ eluted from an Apiezon L column at 150°C but chromatography of the zinc analogue and beryllium oxypropionate was less effective. Cardwell and Carter¹¹⁵ monitored solution reactions between beryllium oxyacetate and oxypropionate, obtaining resolution of mixed oxycarboxylates.

6.2 Pt-bonded transition metal organometallics

The major transition metal organometallic classes studied are those with car-

TABLE 2

ALKYLATION AND ARYLATION DERIVATIZATION REAGENTS FOR GAS CHROMATOGRAPHY OF INORGANICS

From ref. 4, p. 53

Reagent	Derivatization	Ref
Magnesiumdiphenyl	As diethyldithiocarbamate to triphenylarsane	102
Tetramethyltin	$\text{Hg}^{2+} + (\text{CH}_3)_4\text{Sn} \rightarrow \text{CH}_3\text{HgCl} + (\text{CH}_3)_3\text{SnCl}$	106
Phenylmagnesium bromide	Se, Te, Hg, As, Sb, Bi diethyldithiocarbamates to element phenyls	107
Phenylmagnesium bromide	As, Sb thionald ¹¹ to triphenyl CPDS	48
Sodium tetraphenylborate	$4 \text{HgCl}_2 + \text{NaBPh}_4 + 3 \text{H}_2\text{O} \rightarrow 3 \text{HCl} + \text{NaCl} + \text{B}(\text{OH})_3 + \text{PhHgCl}$	108,109
Phenylsulfonic acid	$\text{PhSO}_2\text{H} + \text{HgCl}_2 \rightarrow \text{PhHgCl} + \text{SO}_2 + \text{HCl}$	110
Lithium pentafluorobenzenesulfinate	$\text{Ph-SO}_2\text{Li} + \text{Hg}^{2+} \rightarrow (\text{Ph-SO}_2\text{Hg}^+) \rightarrow \text{SO}_2 + \text{Ph-Hg}^+$	111
4,4-Dimethyl-4-silapentane 1-sulfonate	$\text{Hg}^{2+} + (\text{CH}_3)_3\text{-Si}-(\text{CH}_2)_3\text{-SO}_3\text{Na}$ to CH_3Hg derivatives	112
Pentacyanomethylcobaltate(III)	$\text{Hg}^{2+} + [\text{Co}(\text{CN})_5\text{CH}_3]^{3-}$ to HgCH_3^+	109

bonyl, arene and cyclopentadienyl ligand groups. In general, elution characteristics have been favorable with rare on-column degradation or adsorption.

6.2.1 Metal carbonyls and related compounds

Pommier and Guiochon¹¹⁶ obtained effective separation of $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ on Apiezon L and squalane at 90°C . Satisfactory methods are feasible for the highly toxic $\text{Ni}(\text{CO})_4$ whose high volatility permits elution at low temperatures.

More extensive results are available for arene, cyclopentadienyl and related derivatives of metal carbonyls. Veening *et al.*¹¹⁷ resolved alkyl substituted derivatives of benzenechromiumtricarbonyl. Segard *et al.*¹¹⁸ developed such separations obtaining good separation of isomeric compounds, and Van der Heuvel *et al.*¹¹⁹ used GC-mass spectroscopy for eluate confirmation. Thiophenechromiumcarbonyls however proved rather less chromatographically stable than the arenes¹²⁰.

Manganese group elements form some thermally stable volatile carbonyl derivatives. Cyclopentadienylmanganetricarbonyl [$\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$] and its analogues for example are readily quantitated, a method for the packed column determination of methylcyclopentadienylmanganetricarbonyl [$\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$, MMT] in gasoline with d.c. argon plasma emission specific element detection being reported¹²¹, low nanogram determination was possible.

Other detection methods have also been used for low level determination of MMT. DuPuis and Hill¹²² used a hydrogen atmosphere flame ionization detector to determine $1.7 \cdot 10^{-14}$ g/sec of manganese. Qumby *et al.*⁹⁶ obtained a detection limit of $2.5 \cdot 10^{-13}$ g/sec of manganese with an atmospheric pressure microwave induced helium plasma detector.

Capillary GC has been effective for compounds of this type, specific element detection enhances these separations and gives proof of complete elution. A separation of a group of compounds containing different metals and functionalities, is shown in Fig. 5¹²³. The column was a methylsilicone wall-coated fused-silica capillary. Chromatogram 5 (left) includes six peaks with "carbon" channel of a MIP detector to give "universal" detection. The identities of the eluted peaks are (a) $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$, (b) $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$, (c) $\text{C}_5\text{H}_5\text{Cr}(\text{NO})(\text{CO})_2$ and $(\text{C}_5\text{H}_5)_2\text{Ni}$ (unresolved), (d) $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$, (e) $(\text{C}_5\text{H}_5)_2\text{Fe}$ and (f) $\text{C}_5(\text{CH}_3)_5\text{Co}(\text{CO})_2$. Chromatogram 5 (right), A shows the sample monitored at 267.7 nm for chromium and 5 (right), B shows the two manganese compounds detected at 257.6 nm.

The chromatographic behavior of the previously unchromatographed vanadium and cobalt compounds is excellent and the relatively unstable nickelocene $(\text{C}_5\text{H}_5)_2\text{Ni}$ is also eluted undecomposed. Such results suggest possibilities for GC of a wider range of compound types than its often surmised.

Forbes *et al.*¹²⁴ separated relatively unstable dienetricarbonyliron compounds at $50\text{--}80^\circ\text{C}$ including derivatives of cyclopentadiene, cyclohexa-1,3-diene, cyclohepta-1,3-diene, cycloocta-1,3-diene, cycloocta-1,5-diene, cycloheptatriene and tropone. A recent capillary column separation has been of the cyclopentadienyldicarbonylnitrosyl compounds of tungsten, molybdenum and chromium¹²⁵ which are of interest as polymerization catalysts.

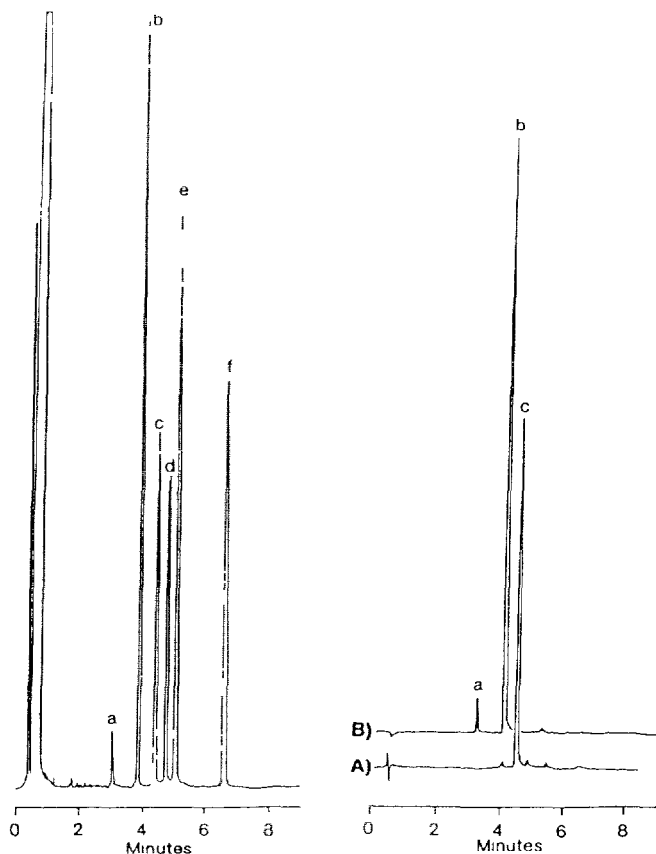


Fig 5 Specific element atmospheric pressure microwave induced plasma detection of organometallics Left chromatogram, carbon monitored at 247.9 nm Right chromatogram(s), (A) chromium monitored at 267.7 nm, (B) manganese monitored at 257.6 nm Peak identities (a) $C_5H_5Mn(CO)_3$, (b) $CH_3C_5H_4Mn(CO)_3$, (c) $(C_5H_5)_2Ni$ and $C_5H_5Cr(NO)(CO)_2$, (d) $C_5H_5V(CO)_4$, (e) $(C_5H_5)_2Fe$, (f) $C_5(CH_3)_5Co(CO)_2$ (From ref. 123)

6.2.2 Metallocenes and their derivatives

Parallel developments have occurred for metallocene separation, ferrocene (biscyclopentadienyl)iron, $(C_5H_5)_2Fe$, being a good example with excellent GC properties.

Arakawa and Tanikawa¹²⁶ and Ayers *et al.*¹²⁷ resolved ferrocene derivatives with alkyl, vinyl, dialkyl, acetyl, diacetyl and hydroxymethyl substituents. Little capillary GC has been reported but is clearly viable, a capillary separation of ferrocene, ruthenocene and osmocene was obtained at 150°C¹²⁵.

6.2.3 Metal chelates

Metal chelates having the charge on the central metal atom neutralized by equal and opposite charge on anionic ligands with oxygen, nitrogen, sulfur or phosphorus donor atoms, are an important complex class. For GC the features determining if the separation of such compounds is viable are a suitable combination of

volatility and thermal stability and sufficient shielding of the metal from undesirable column interactions. The range of organic ligands suitable for GC analysis is limited but considerable development and application is recorded.

6.2.3.1 Beta-diketonates In 1955 Lederer¹²⁸ suggested neutral chelate complexes to possess adequate vapor phase thermal stability to make for GC. Acetylacetonates first received attention because of their ready formation and high stability which results from multiple chelate rings. Metallic ions with coordination numbers equal to twice their oxidation state such as Al(III), Be(II) and Cr(III) form coordinatively saturated neutral acetylacetonates and chromatograph well¹²⁹. Cu(II), Ni(II) and other chelates which are not coordinatively saturated tend to solvate, polymerize or undergo undesirable adsorption, thus limiting GC utility. Non-fluorinated beta-diketonates in general have inadequate thermal and chromatographic stability for on-column degradation to be absent, little quantitative work has thus been attempted for these complexes.

The major breakthrough in chelate GC was the development of fluorinated beta-diketonates which show greater volatility and thermal stability. Moshier and Sievers¹³⁰ provided the thrust, and their monograph published in 1965 summarizes analytical progress. Trifluoroacetylacetone [1,1,1-trifluoro-2,4-pentanedione (HTFA)] and hexafluoroacetylacetone [1,1,1,5,5,5-hexafluoro-2,4-pentanedione (HHFA)] have been the most widely exploited ligands. HTFA extended the range of metals gas chromatographed with minimal decomposition to Ga(III), In(III), Sc(III), Rh(III) and V(IV)¹³¹. Some HTFA complexes such as Cu(TFA)₂ however elute poorly below the microgram level, showing on-column degradation. Sokolov used radioactive ⁶⁴Cu tagging to follow anomalous sorption¹³². It has been shown that Th(TFA)₄, U(TFA)₄ and Fe(III)(TFA)₃ degrade under typical GC conditions but give better peak shapes and elution limits if HTFA vapor is added to the carrier gas¹³³ to reduce chelate dissociation.

Trifluoroacetylacetonates of trivalent hexacoordinate metals such as Cr(III), Co(III), Al(III) and Fe(III) have facial (*cis*) and meridional (*trans*) geometric isomer forms which interconvert at elevated temperatures. Below 100°C this occurs slowly enough for chromium chelates to be eluted independently, but exchange of aluminum complexes isomers is rapid and only the more stable meridional form is seen.

These are illustrated in a high resolution capillary separation of Sucre and Jennings¹³⁴ shown in Fig. 6. The facial and meridional Cr(TFA)₃ chelates are clear as is the single peak for Al(TFA)₃. The disruption of the baseline before elution of Cu(TFA)₂ confirms on-column degradation even in the relatively inert fused-silica column.

The many analytical applications of HTFA chelates are reviewed in detail by Moshier and Sievers¹³⁰, by Uden and Henderson¹³⁵, Rodriguez-Vazquez¹³⁶ and in the books by Guiochon and Pommier³ and Schwedt⁴. Among recent applications have been analysis for beryllium in ambient air particulates¹³⁷. After glass fiber filter sampling extraction and chelation, packed column chromatography with electron-capture detection gave quantitation in collected particulates at levels of 2–20 × 10⁻⁵ μg of beryllium per cubic meter in the sampled air. The effects of ligand doping in the carrier gas on the GC of Cr(TFA)₃ and Fe(TFA)₃ have been studied¹³⁸.

Hexafluoroacetylacetonate complexes (HHFA), have been also extensively studied. Their great volatility and low solubility in most stationary phases cause short

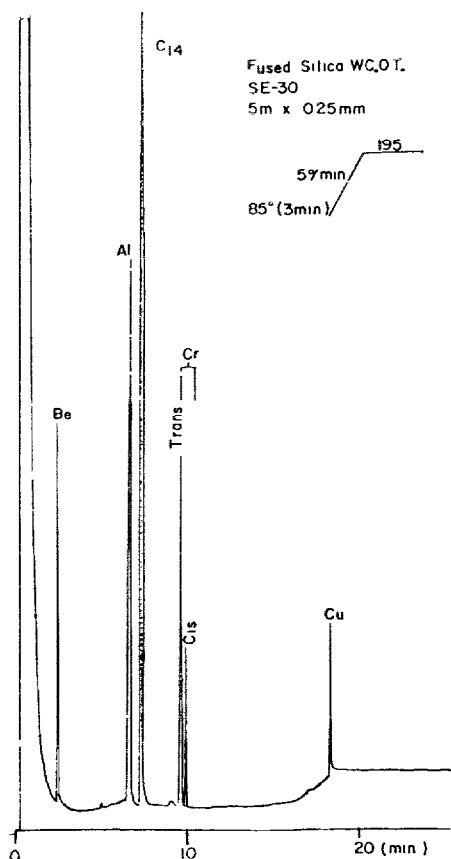


Fig 6 Capillary separation of Be, Al, Cr and Cu trifluoroacetylacetonates and *n*-tetradecane Inlet split 100:1 Fused-silica WCOT SE-30, 5 m × 0.25 mm ID Temperature program, 85–195°C at 5°C/min Hydrogen carrier gas (From ref 134)

retention times at low column temperatures and their great electron capturing ability has allowed extremely low detection limits to be obtained for $\text{Cr}(\text{HFA})_3$ and $\text{Be}(\text{HFA})_2$ ¹³⁹ Quantitative derivatization may be difficult because of hydrate formation of the ligand and complexes Comparative determination of chromium by AA, TFA and HFA was recently reported¹⁴⁰

As modifications to the beta-diketone structure are straightforward, various derived chelating ligands have been evaluated for GC applications Two major adaptations are replacement of the methyl group by branched alkyl groups, particularly *tert*-butyl, and the incorporation of perfluoroalkyl groups in the ligand While some perfluorinated long chain ligands such as 1,1,1,2,2,3,3,7,7,7-decafluoroheptanedione (HDFHD) have been employed synergically with dibutylsulfoxide for extraction and GC of $\text{U}(\text{VI})\text{O}_2$, Th(IV) and the lanthanides¹⁴¹, their difficult preparation and facile hydration have prevented extensive adoption

The most extensive development has been for diketones having both a *tert*-butyl and a long chain fluoroalkyl group Springer *et al*¹⁴² used 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione [heptafluoropropanoylpivalylmethane

(HFOD or HHPM)] for lanthanide separations This and similar ligands with other fluoroalkyl groups have been applied to a range of analytical procedures and preparative separations Fontaine *et al*¹⁴³ separated Th(FOD)₄, U(FOD)₄ and U(FOD)₆, but lead chelates showed some on-column degradation¹⁴⁴ Similar behavior was obtained for alkali metal¹⁴⁵, alkaline earth¹⁴⁶ and mixed chelates of the form MM'L₄ where M is an alkali metal and M' a rare earth¹⁴⁷ These studies, although of limited success, emphasize application of these ligands for GC of all metal groups

A recent high resolution fused-silica capillary study separated 24 of 25 possible mixed ligand Cr(III) complexes¹⁴⁸ Linear retention volumes were noted with respect to the carbon number of the central or the terminal ligand alkyl groups

6.2.3.2 *Other beta-difunctional ligands* Despite the wide application of beta-diketonates a logical approach to problems of stability, monomer integrity and selective metal reactivity resides in alternative ligands obtained by substitution of donor oxygen atoms with sulfur or nitrogen atoms The major classes of such ligands are summarized¹³⁵ in the diagram in Fig 7, which shows the formation of bidentate

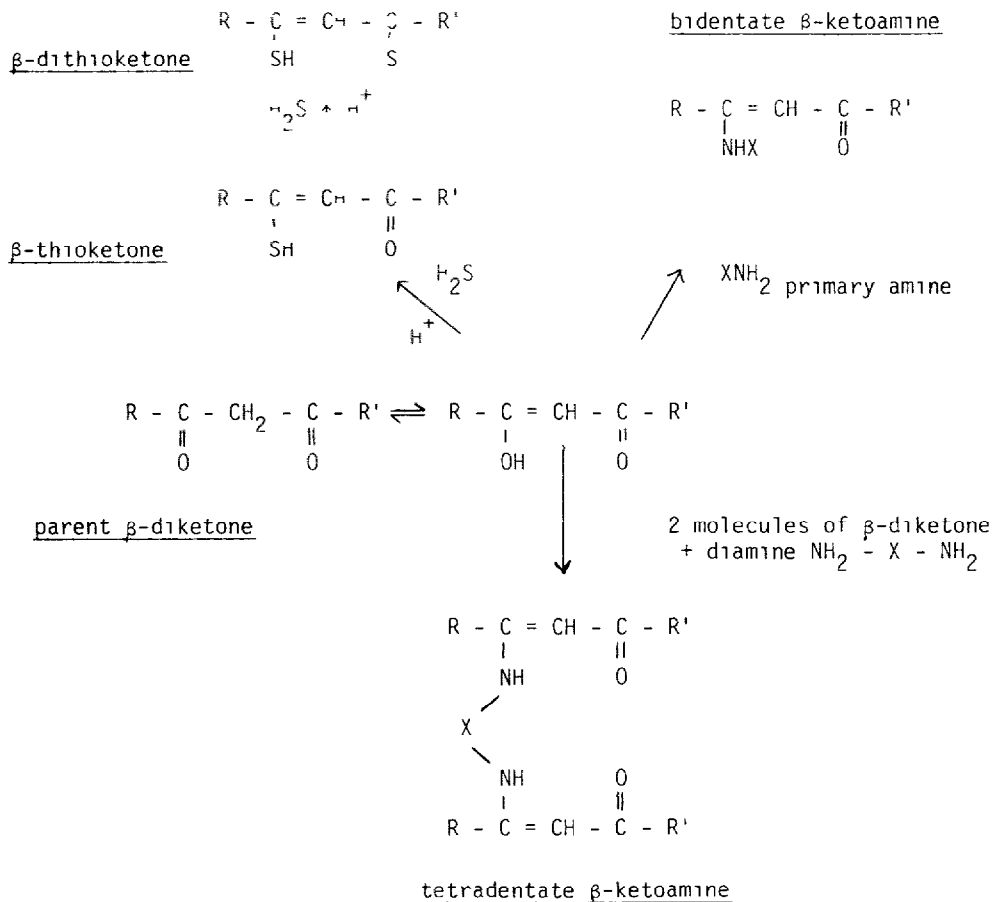


Fig 7 Formation of major beta-difunctional ligands for metal complex GC (From ref 135)

ligands with sulfur donors and bidentate and tetradentate ligands with nitrogen donors

Beta-thioketonates Despite minimal structural changes on replacement of oxygen with sulfur, the preference of β -thioketonates for "soft" class B metals such as nickel, complements the preferred complexation of oxygen ligands for "hard", such as aluminum and chromium. Although preparation may be difficult, there are some advantages of these chelates for GC since the metals with good behavior are those for which the diketonates are unsatisfactory, e.g., nickel, palladium, platinum, zinc and cobalt. There is also the possibility of simultaneous determination of cobalt in both II and III oxidation states since Co(II) bis(monothioacetylacetonate) and Co(III) tris(monothio trifluoroacetylacetonate) have been chromatographed independently^{149,150}. Nickel has been determined quantitatively as the monothio trifluoroacetylacetonate and such determinations for palladium and platinum are feasible.

Nickel bis(dithioacetylacetonate) has been shown more stable chromatographically than the monothio analogue and has been eluted quantitatively at the 10–20 ng level¹⁵¹.

Beta-ketoaminates Bidentate and tetradentate β -ketoaminates (β -aminoketonates) of some transition metals have been gas chromatographed, in general, the nitrogen donor atom gives an intermediate place between betadiketones and monothioketones for metals which are readily complexed with a somewhat closer correspondence with the latter. The nickel group of metals is favorably complexed as are those of copper(II) and vanadyl [V(IV)O]. The bidentate ketoamines have been of limited utility being restricted to submicrogram elution on packed columns¹⁵², but inert capillary columns may allow trace quantitative elution permitting the rapid formation rates for these complexes to be exploited.

The tetradentate beta-ketoamine ligands are very useful for GC of divalent transition metals. The addition of the third (five-membered) chelate ring affords great stability which offsets the lower volatility than that of the analogous bidentate chelates. Table 3 shows the tetradentate betaketoamine ligands applied for GC of copper, nickel, palladium and vanadyl complexes. In contrast to all bidentate beta-difunctional ligand complexes for the tetradentates, the fluorinated chelates show lower volatilities than their non-fluorinated analogues, this allows the latter to be readily gas chromatographed since lower column temperatures may be used¹⁵³.

The fluorinated chelates have high electron-capturing ability¹⁵⁷ giving pg detection but the complexes form more slowly than the non-fluorinated ones which are also detectable by ECD to the 100-pg level. The ligands $H_2(enAA_2)$ and $H_2(pnAA_2)$ were thus used for determination of trace palladium in nickel and copper based ores¹⁵⁴. Belcher *et al*¹⁵⁹ described the simultaneous determination of copper and nickel by solvent extraction and GC of complexes of $H_2(enAPM_2)$. Dilli and co-workers have examined the chemistry and GC of this series of complexes in great detail, their studies including analysis of preparative procedures¹⁶², reaction chemistry^{161, 163}, and simultaneous determination of copper, nickel and vanadium at the 5-pg level as $H_2(pnTFA_2)$ complexes. Dilli and Patsalides¹⁶² showed that the very high relative volatility of the $H_2(enTPM_2)$ complexes accompanied structures with trifluoromethyl substituent groups adjacent to the diamine bridge and not remote from it as in other ligands of this class.

GC has been useful for chelate structural studies as in the straightforward

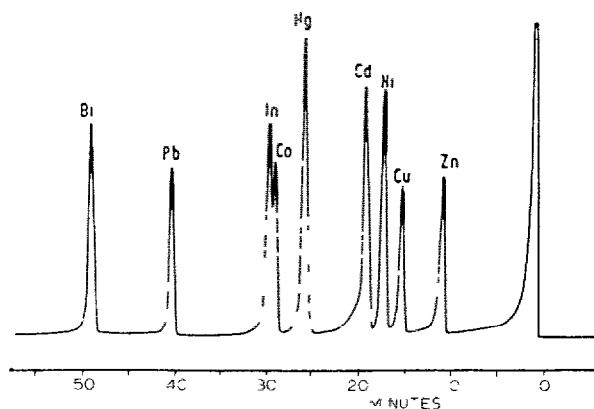


Fig 8 Separation of zinc, copper(II), nickel, cadmium, mercury, cobalt(II), indium, lead and bismuth di(trifluoroethyl)dithiocarbamates Column, 90 cm \times 2 mm 3% OV-25 on Chromosorb W HP, 100-120 mesh Temperature program, 120-210°C at 2°C/min (From ref 177)

Predictably fluorinated dialkyldithiocarbamates have also been subject to analytical attention because of their greater volatility than the non-fluorinated analogues Tavlaridis and Neeb¹⁷⁶ separated zinc, nickel, cadmium, lead, antimony and bismuth di(trifluoroethyl)dithiocarbamates at 185°C on a packed methylsilicone column

A packed column temperature programmed separation from 120 to 210°C is shown in Fig 8¹⁷⁷ Recent reports have described element analysis using these chelates^{178,179}

Lithium bis(trifluoroethyl)dithiocarbamate is a useful reagent to prepare these

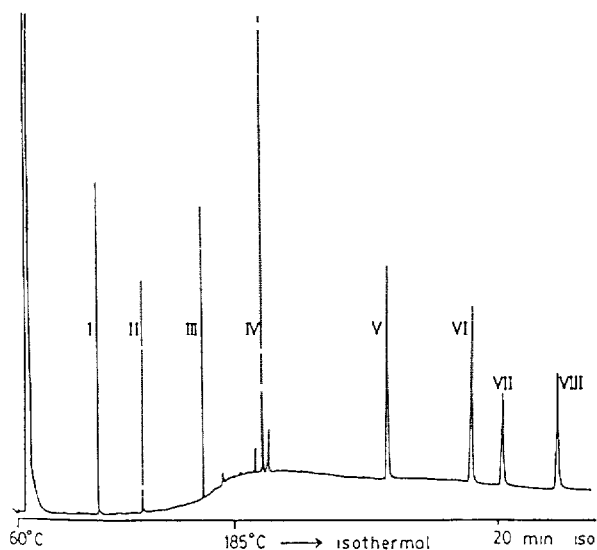


Fig 9 Fused-silica capillary chromatogram of alkanes and metaldisopropylidithiophosphinates Column, 25 m \times 0.3 mm OV 1 Hydrogen carrier gas at 57 cm/sec Temperature program, 60-185°C FID detection Peak identities I = n -C₁₂, II = n -C₁₄, III = n -C₁₇, IV = n -C₂₀, V = Ni chelate, VI = n -C₂₄, VII = Pd chelate, VIII = Pt chelate (From ref 184)

chelates as it can be made in high purity and yield¹⁸⁰ Sucre and Jennings¹³⁴ reported good capillary separation of nickel and cobalt(III) chelates on 5-m fused-silica columns with a 150–190°C temperature program It is possible that further refinement of high-resolution columns will broaden the application of these complexes for analytical GC

6 2 3 4 Dialkyldithiophosphinates The gas chromatography of dialkyldithiophosphinate (dithiophosphate) complexes has paralleled that of the dialkyldithiocarbamates Cardwell and McDonagh¹⁸¹ showed packed column separation of zinc, nickel, palladium and platinum chelates of O,O'-dialkyldithiophosphinates Kleinmann and Neeb¹⁸² reported similar study for zinc, cadmium and lead complexes Feigler *et al*¹⁸³ developed quantitation of cadmium at concentrations in the range of 0.03–0.3 ppm in water These complexes are usefully detected by flame photometry monitoring either the S₂ or HPO emission modes, with sensitivities rather better than flame ionization detection A capillary column separation of alkanes and metal diisopropylidithiophosphinates is shown in Fig 9¹⁸⁴ with very good peak shape for nickel, palladium and platinum complexes

6 2 3 5 Metalloporphyrins An important demonstration of the enhanced scope of inorganic applications available with inert high-resolution fused-silica capillary columns is the conventional GC of transition metal porphyrin complexes Some separation of metalloporphyrins had been achieved by hyperpressure supercritical fluid chromatography¹⁸⁵ but they were considered too non-volatile for GC Marriott *et al*¹⁸⁶ however, achieved capillary GC of these closed macrocyclic ring complexes although Kovats indices from 5200 to 5600 necessitated short (6 m) columns In Fig

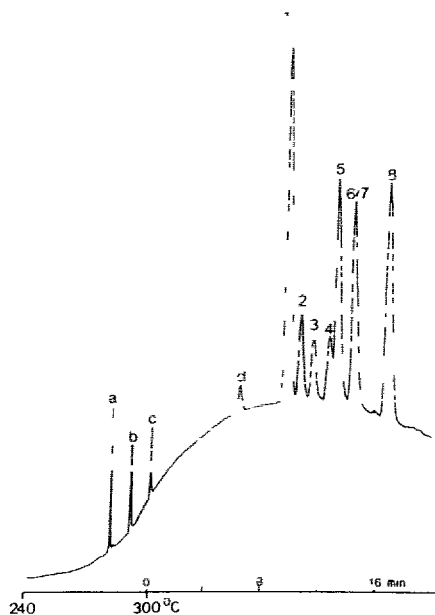


Fig 10 Fused-silica capillary chromatogram of alkanes and metalloporphyrins Column, 6 m \times 0.3 mm OV 1 Temperature program, 60–300°C at 7°C/min Peak identities a = *n*-C₄₀, b = *n*-C₄₂, c = *n*-C₄₄, d = *n*-C₅₀, 1 = Cu Aetio, 2 = Ni Aetio, 3 = VO Aetio, 4 = Co Aetio, 5 = Cu OEP, 6 = Ni OEP, 7 = VO OEP, 8 = Co OEP (From ref 186)

10 is shown a chromatogram of *n*-alkanes and metalloporphyrins, the first four peaks corresponding to *n*-alkanes in the C₄₀-C₅₀ range and the later peaks to copper, nickel, vanadyl and cobalt aetioporphyrin I and octaethylporphyrin chelates. Elution of all peaks was in the isothermal 300°C region. A parallel study involved capillary GC of bis(trimethylsiloxy)silyl derivatives of porphyrins with polar ester side-chains¹⁸⁷

7 EMISSION SPECTROSCOPIC DETECTION IN INORGANIC GC

When an eluted GC peak contains a particular element not present in other components of the sample matrix, application of a detector responding solely to that element gives significant simplification since compounds containing that element need only to be resolved from each other and not necessarily from other components in the sample. Inorganic GC applications have benefited from flame photometric detection for sulfur, phosphorus and other elements, and thermionic detection for phosphorus, but the much wider potential of atomic spectral detection methods relying on wavelength selection to impart selectivity has been realized in recent years.

Although the greatest emphasis in developing such detectors has been for non-metallic elements, the quantitation of metal content is also attractive for many applications. Van Loon¹⁸⁸ commented on the limited use of metal specific detection in chromatography but stressed the great potential of atomic absorption spectral detection. Atomic absorption GC detection was described by Kolb *et al*¹⁸⁹ and later by Longbottom⁶² who applied cold vapor analysis for elemental mercury. Parris *et al*¹⁰¹ discussed general factors in the adaptation of atomic absorption furnaces for GC detection. As noted earlier in the review, lead specific detection in particular has been aided by AAS⁸⁹⁻⁹³.

In contrast to AAS, atomic emission spectroscopy (AES) has the advantage of being a multi-element technique which frequently has a linear dynamic range of five or six orders of magnitude. The advent of various accessible plasma sources, particularly in combination with high-resolution monochromators to minimize spectral interferences, has produced a resurgence of analytical applications, not least in chromatographic detection. Limited success has been achieved in flame emission GC interfacing¹⁹⁰ but it suffers from limited elemental applicability, modest sensitivity and frequent spectral interferences. By contrast, plasma sources can overcome most of these disadvantages and have attracted increasing attention. The three major sources used in GC detection have been the microwave induced and sustained helium plasma (low or atmospheric pressure) (MIP), the d.c. argon plasma (DCP) and the inductively coupled argon plasma (ICP).

The major advantages of interfaced GC-plasma emission spectroscopy are the following:

- (a) The ability to perform speciation, either prior to or within the chromatographic column for many metals and non-metals, directly or through derivatization.
- (b) The ability to tolerate non-ideal chromatographic elution. The specificity of plasma emission enables the analyst to tolerate incomplete resolution, frequent in complex matrices.
- (c) The typical high sensitivity achieved.
- (d) The multielement capacity in atomic emission.
- (e) The compatibility with existing GC systems with simple interface devices.

7.1 *The microwave induced helium plasma detector (MIP)*

The first effective atmospheric pressure GC-MIP system was designed by McCormack *et al*¹⁹¹ using an argon plasma induced and sustained by the usual 2.45-GHz microwave source. Bache and Lisk¹⁹² used a reduced pressure helium plasma GC detector as did Talmi^{48,193} for mercury, arsenic and antimony compounds. A range of transition and main group metal diketonates were detected by Kawaguchi *et al*¹⁹⁴ and Dagnell *et al*¹⁹⁵. The most comprehensive reduced pressure GC-MIP data is that of McLean *et al*¹⁹⁶ who used at 0.25 torr, 100–200 W 2.45 GHz plasma. Detection limits were quoted from 0.03 ng/sec for hydrogen to 3.0 ng/sec for oxygen.

A major practical advance in GC-MIP was made by utilizing Beenakker's TM₀₁₀ cylindrical resonance cavity which permits an atmosphere pressure helium plasma to be maintained at the same low power as for reduced pressure plasmas. GC systems using this cavity are described in detail^{33,96,99} and applications have been noted earlier in this review (Fig. 4, ref. 73, Fig. 5, ref. 123). In general detection limits for 30 elements are in the low pg/s range. The general area of GC-MIP has been subject to recent review^{61,197}.

7.2 *The d.c. argon plasma (DCP)*

The wide adoption of the atmospheric pressure d.c. argon plasma as a spectral source encouraged interfacing for GC detection. A configuration suitable for packed column application was described by Lloyd *et al*¹⁹⁸. This was used for the determination of methylcyclopentadienylmanganese tricarbonyl in gasoline¹²¹ and other applications with both a two-electrode and a three-electrode plasma. The energetics of the argon plasma give detection limits in GC-DCP for many metals within an order of magnitude of the best GC-MIP data although emission intensities from many non-metals (except silicon and boron) are very much lower.

7.3 *The inductively coupled argon plasma (ICP)*

In comparison with the MIP and the DCP, the ICP has been little utilized as a GC detector, but in view of the great popularity of the technique it may be developed in the future. An elemental analysis procedure for empirical formula determination by GC-ICP was reported by Windsor and Denton¹⁹⁹ who obtained detection in the low ng range for metals and some non-metals. Sommer and Ohls²⁰⁰ investigated GC-ICP with a higher power nitrogen-argon system with emphasis on lead and silicon compounds.

8 THE PAST AND FUTURE OF INORGANIC GC

The range of application of inorganic GC described in this review emphasizes the scope of this technique to be much wider than is often realized. While the history of inorganic GC has mirrored that of the discipline in general, the developments of recent years have greatly widened areas of application. The most important advances which will continue to affect inorganic GC are (i) The development of inert silica

capillary columns with very low levels of reactive residual metal impurities, the absence of interactive stationary phase supports plays a major part in quantities elution of inorganics (ii) The parallel development of capillary columns with high temperature limits (iii) The rapid development of specific element atomic spectral detection to give high sensitivity detection of inorganic species even in complex unresolved eluent profiles

Inorganic GC has yet much to offer the analytical chemical scientist

REFERENCES

- 1 A V Kiselev and Y I Yashin, *Gas Adsorption Chromatography*, Plenum Press, New York, London, 1969
- 2 O L Hollis, *J Chromatogr Sci*, 11 (1973) 335
- 3 G Guiochon and C Pommier, *Gas Chromatography in Inorganics and Organometallics*, Ann Arbor Science Publ, Ann Arbor, MI, 1973
- 4 G Schwedt, *Chromatographic Methods in Inorganic Analysis*, Huthig, Heidelberg, 1981
- 5 J King and S W Benson, *J Chem Phys*, 44 (1966) 1007
- 6 R Aubeau, L Leroy and L Champeix, *J Chromatogr*, 19 (1965) 249
- 7 J E Purcell, *Nature (London)*, 201 (1964) 1321
- 8 C T Hodges and R F Matson, *Anal Chem*, 37 (1965) 106
- 9 G M Neumann, *Z Anal Chem*, 244 (1969) 302
- 10 O L Hollis and W V Hayes, *J Gas Chromatogr*, 4 (1966) 235
- 11 E L Obermuller and G O Charlier, *J Chromatogr Sci*, 7 (1969) 580
- 12 R L Hoffmann, G R List and C D Evans, *Nature (London)*, 211 (1966) 965
- 13 A G Datar, P S Ramanathan and M Sankar Das, *J Chromatogr*, 106 (1975) 428
- 14 R Ellerker, F Lax and H J Dee, *Water Res*, 1 (1967) 243
- 15 R V Holland and P W Board, *Analyst (London)*, 101 (1976) 887
- 16 K L McDonald, *Anal Chem*, 44 (1972) 1298
- 17 H W Kohlschutter and W Hoppe, *Z Anal Chem*, 197 (1963) 133
- 18 G Manara and M Taramasso, *J Chromatogr*, 77 (1973) 109
- 19 A G Datar, P S Ramanathan and M Sankar Das, *J Chromatogr*, 93 (1974) 217
- 20 O Pitak, *Chromatographia*, 2 (1969) 462
- 21 A Steffen and K Bachmann, *Talanta*, 25 (1978) 551
- 22 W A Robbins and J A Caruso, *J Chromatogr Sci*, 17 (1979) 360
- 23 G Rambeau, *Chim Anal*, 52 (1970) 774
- 24 R P Hirschmann and T L Mariani, *J Chromatogr*, 34 (1968) 78
- 25 M L Conti and M Lesimple, *J Chromatogr*, 29 (1967) 32
- 26 H W Durbeck and R Niehaus, *Chromatographia*, 11 (1978) 14
- 27 J S Fritz and R C Chang, *Anal Chem*, 46 (1974) 939
- 28 R D Kadeg and G D Christian, *Anal Chim Acta*, 88 (1977) 117
- 29 T L C deDouza and S P Bhatia, *Anal Chem*, 48 (1978) 2234
- 30 J Koch and K Figge, *J Chromatogr*, 109 (1975) 89
- 31 G Parissakis, D Vrandit-Piscon and J Kohtoyannakos, *Z Anal Chem*, 254 (1971) 188
- 32 O Pitak, *Chromatographia*, 2 (1969) 304
- 33 J L Genna, W D McAninch and R A Reich, *J Chromatogr*, 238 (1982) 103
- 34 J J Kaufman, J E Todd and W S Koski, *Anal Chem*, 29 (1957) 1032
- 35 E J Sowinski and I H Suffet, *Anal Chem*, 44 (1972) 2237
- 36 E J Sowinski and I H Suffet, *Anal Chem*, 46 (1974) 1218
- 37 P L Timms, C C Simpson and C S G Phillips, *J Chem Soc*, (1964) 1467
- 38 F Feher and H Strock, *Naturwissenschaften*, 50 (1963) 570
- 39 F H Pollard, G Nickless and D J Cooke, *J Chromatogr*, 13 (1964) 48
- 40 C J Soderquist and D G Crosby, *Anal Chem*, 50 (1978) 1435
- 41 A. D. Золот. G. G. Девятых, V. Y. Дудуров and A. M. Амелсченко, *Russ J Inorg Chem*, 9 (1964) 1364
- 42 R D Kadeg and G D Christian, *Anal Chim Acta*, 88 (1977) 117

- 43 T Dumas and E J Bond, *J Chromatogr*, 206 (1981) 384
44 W B Robbins and J A Caruso, *J Chromatogr Sci*, 17 (1979) 360
45 M H Hahn, K J Mulligan, M E Jackson and J A Caruso, *Anal Chim Acta*, 118 (1980) 115
46 P R Gifford and S Bruckenstein, *Anal Chem*, 52 (1980) 1028
47 Y Talmi and D T Bostick, *Anal Chem*, 47 (1975) 2145
48 Y Talmi and V E Norvell, *Anal Chem*, 47 (1975) 1510
49 S T Sie, J P A Bleumer and G W A Rijnders, *Sep Sci*, 1 (1966) 41
50 R S Juvet and F M Wach, *Anal Chem*, 32 (1960) 290
51 C Pommier, C Eon, H Fould and G Guiochon, *Bull Soc Chim Fr*, (1969) 1401
52 I Tohyama and K Otazai, *Z Anal Chem*, 262 (1972) 346
53 F Dienstbach and K Bachmann, *Anal Chem*, 52 (1980) 620
54 G Michael, U Danne and G Fischer *J Chromatogr*, 118 (1976) 104
55 T R Crompton, *Gas Chromatography of Organometallic Compounds*, Plenum Press, New York, 1982
56 S Tsalas and K Bachmann, *Talanta*, 27 (1980) 201
57 R S Juvet and R L Fisher, *Anal Chem*, 38 (1966) 1860
58 A Steffen and K Bachmann, *Talanta*, 25 (1978) 51
59 G L Baughman, M H Carter, N L Wolf and R G Zepp, *J Chromatogr* 76 (1973) 471
60 C A Bache and D J Lisk, *Anal Chem*, 43 (1971) 950
61 T H Risby and Y Talmi, *C R C Critical Reviews in Analytical Chemistry*, 14, No 3 (1983) 231
62 J E Longbottom, *Anal Chem*, 44 (1972) 1111
63 G W Rice, J J Richard, A P D'Silva and V A Fassel, *Anal Chem*, 53 (1981) 1519
64 M Shaviat, *J Chromatogr Sci*, 17 (1979) 527
65 R Belcher, J A Rodriguez-Vazquez, P C Uden and W L I Stephen, *Chromatographia*, (1976) 201
66 G Schomberg, R Koster and D Henneberg, *Z Anal Chem*, 170 (1959) 285
67 R Koster and G Bruno, *Ann Chem*, 629 (1960) 89
68 L J Kuhns, R S Braman and J E Graham, *Anal Chem*, 34 (1962) 1700
69 J Stuchlik and V Paoakova, *J Chromatogr*, 174 (1979) 224
70 Y N Bortnikov, E N Vyankin, E N Gladyshev and V S Andreevichev, *Zavodsk Lab*, 35 (1969) 1445
71 P Longi and R Mazzochi, *Chimica Ind Milano*, 48 (1966) 718
72 K K Fukin, V G Rezhnikov, T S Kuznetsova and I A Frolov, *Zavodsk Lab*, 39 (1973) 993
73 J Frank and M Wurst, *Coll Czech Chem Commun*, 25 (1960) 701
74 S A Estes, C A Poirer, P C Uden and R M Barnes, *J Chromatogr*, 196 (1980) 265
75 K R Burson and C T Kenner, *Anal Chem*, 41 (1969) 820
76 M Wurst and J Churacek *Coll Czech Chem Commun*, 36 (1971) 3497
77 F H Pollard, G Nickless and P C Uden, *J Chromatogr*, 19 (1965) 28
78 G N Bortnikov, A V Kiselev, N S Vyazankin and Ya I Yashin, *Chromatographia*, 4 (1971) 14
79 F H Pollard, G Nickless and D J Cooke, *J Chromatogr*, 17 (1965) 472
80 C G Flinn and W A Aue, *J Chromatogr* 186 (1979) 299
81 S Kapila and C R Vogt, *J Chromatogr Sci*, 181 (1980) 144
82 D R Hansen, T J Gilfoil and H H Hill, Jr, *Anal Chem*, 53 (1981) 857
83 J A Rodriguez-Vazquez, *Talanta*, 25 (1978) 299
84 P T S Wong, Y K Chan and P L Luxon, *Nature (London)*, 253 (1975) 263
85 U Schmidt and F Huber, *Nature (London)*, 259 (1976) 159
86 W A Aue and H H Hill, Jr, *J Chromatogr*, 74 (1972) 319
87 M D DuPuis and H H Hill, Jr, *Anal Chem* 51 (1979) 292
88 P M Mutsaers and J E Van Steen *J Inst Petrol*, 58 (1972) 102
89 P R Ballinger and I M Whittemore, *Proc Amer Chem Soc, Div of Petroleum Chemistry, Atlantic City, NJ*, 13 (1968) 133
90 Y K Chau, P T S Wong and P D Goulden, *Anal Chim Acta*, 85 (1976) 421
91 Y K Chau P T S Wong, G A Bengert and O Kramar, *Anal Chem*, 51 (1979) 186
92 B Y T Radzwick, J C Van Loon and Y K Chau, *Anal Chim Acta*, 255 (1979) 105
93 J W Robinson, E L Diesel, J P Goodbreed, R Bliss and R Marshall, *Anal Chim Acta*, 92 (1977) 321
94 D C Reamer, W H Zoller and T C O'Haver, *Anal Chem*, 50 (1978) 1449
95 C I M Beenakker, *Spectrochim Acta*, 31B (1976) 483

- 96 B D Qumby, P C Uden and R M Barnes, *Anal Chem*, 50 (1978) 2112
97 S A Estes, P C Uden and R M Barnes, *J Chromatogr*, 239 (1982) 181
98 S A Estes, P C Uden and R M Barnes, *Anal Chem*, 53 (1981) 1336
99 S A Estes, P C Uden and R M Barnes, *Anal Chem*, 54 (1982) 2402
100 B J Gudzinowicz and H F Martin, *Anal Chem*, 34 (1962) 648
101 G E Parris, W R Blair and F E Brinkman, *Anal Chem*, 49 (1977) 378
102 G Schwedt and H A Ruessel, *Chromatographia*, 5 (1972) 242
103 C S Evans and C M Johnson, *J Chromatogr*, 21 (1966) 202
104 Y Talmi and W W Audren, *Anal Chem*, 46 (1974) 2122
105 S A Estes, P C Uden and R M Barnes, *Anal Chem*, 53 (1981) 1829
106 J A Rodriguez-Vazquez, *Talanta*, 25 (1978) 299
107 G Schwedt and H A Russel, *Z Anal Chem*, 264 (1973) 301
108 V Luckow and H A Russel, *J Chromatogr*, 150 (1978) 150
109 P Zarnegar and P Mushak, *Anal Chim Acta*, 69 (1974) 389
110 P Jones and G Nickless, *J Chromatogr*, 76 (1973) 285
111 P Mushak, F E Tibbetts III, P Zarnegar and G B Fisher, *J Chromatogr*, 87 (1973) 215
112 P Jones and G Nickless, *J Chromatogr*, 89 (1974) 201
113 L M Brown and K S Mazdizyasni, *Anal Chem*, 41 (1969) 1243
114 R S Barratt, R Belcher, W I Stephen and P C Uden, *Anal Chim Acta*, 57 (1971) 447
115 T J Cardwell and M R L Carter, *J Chromatogr*, 140 (1977) 93
116 C Pommier and G Guiochon, *J Chromatogr Sci*, 8 (1970) 486
117 H Veening N J Graves, D B Clark and B R Willeford, *Anal Chem*, 42 (1969) 1655
118 C Segard, P P Rogues, C Pommier and G Guiochon, *Anal Chem*, 43 (1971) 1146
119 W J A Van der Heuvel J S Keller, H Veening and B R Willeford, *Anal Lett*, 3 (1970) 279
120 C Segard, C Pommier, B P Rogues and G Guiochon, *J Organomet Chem*, 77 (1974) 49
121 P C Uden, R M Barnes and F P DiSanzo, *Anal Chem*, 50 (1978) 852
122 M D DuPuis and H H Hill, *Anal Chem* 51 (1979) 292
123 S A Estes, P C Uden, M D Rausch and R M Barnes, *J High Resolut Chromatogr Chromatogr Commun*, 3 (1980) 471
124 E J Forbes, M K Sultan and P C Uden, *Anal Lett*, 5 (1972) 927
125 P C Uden, D E Henderson, F P DiSanzo, R J Lloyd and T P Tetu, *J Chromatogr*, 196 (1980) 403
126 K Kanikawa and K Arakawa, *Chem Pharm Bull (Tokyo)*, 13 (1965) 926
127 O E Ayers T C Smith, J D Burnett and B W Ponder, *Anal Chem*, 38 (1966) 1606
128 M Lederer, *Nature (London)*, 176 (1955) 462
129 W J Biermann and H Gesser, *Anal Chem*, 32 (1960) 1525
130 R W Moshier and R E Sievers, *Gas Chromatography of Metal Chelates*, Pergamon, Oxford, 1965
131 R E Sievers, B W Ponder M L Morris and R W Moshier, *Inorg Chem*, 2 (1963) 693
132 D N Sokolov, A V Davydov, S Y Prokofyev, S S Travnikov, E V Fedoseev and B F Myasoedov, *J Chromatogr*, 155 (1978) 241
133 T Fujinaga, T Kuwamoto and S Murai, *Talanta*, 18 (1971) 429
134 L Sucre and W Jennings *J High Resolut Chromatogr Chromatogr Commun*, 3 (1980) 452
135 P C Uden and D E Henderson, *Analyst (London)*, 102 (1977) 889
136 J A Rodriguez-Vazquez, *Anal Chim Acta*, 73 (1974) 1
137 W D Ross, J L Pyle and R E Sievers, *Environ Sci Technol*, 11 (1977) 469
138 K W M Siu, M E Fraser and S S Berman, *J Chromatogr*, 256 (1983) 455
139 M L Morris, R W Moshier and R E Sievers, *Inorg Chem*, 2 (1963) 411
140 U Bendig, H Stenner and A Kettrup, *Z Anal Chem*, 309 (1981)
141 C A Burgett and J S Fritz, *J Chromatogr* 77 (1973) 265
142 C S Springer jr, D W Meek and R E Sievers, *Inorg Chem*, 6 (1967) 1105
143 R Fontaine, B Santoni, C Pommier and G Guiochon, *Chromatographia*, 3 (1970) 532
144 R Belcher, J R Majer, W I Stephen, I J Thomson and P C Uden, *Anal Chim Acta*, 50 (1970) 423
145 R Belcher J R Majer, R Perry and W I Stephen, *Anal Chim Acta*, 45 (1970) 305
146 R Belcher, R C Cranley J R Majer, W I Stephen and P C Uden, *Anal Chim Acta*, 60 (1972) 109
147 R Belcher J R Majer, R Perry and W I Stephen, *J Inorg Nucl Chem*, 31 (1969) 47

- 148 R E Sievers and K C Brooks, *Int J Mass Spectrom Ion Phys*, 47 (1983) 527
- 149 R Belcher, W I Stephen, I J Thomson and P C Uden, *J Inorg Nucl Chem*, 33 (1971) 1851
- 150 R Belcher, W I Stephen, I J Thomson and P C Uden, *J Inorg Nucl Chem*, 34 (1972) 1017
- 151 P C Uden, K A Nonnemaker and W E Geiger, *Inorg Nucl Chem Lett*, 14 (1978) 161
- 152 R Belcher, R J Martin, W I Stephen, D E Henderson, A Kamalizad and P C Uden, *Anal Chem*, 45 (1973) 1197
- 153 R Belcher, K Blessel, T J Cardwell, M Pravica, W I Stephen and P C Uden, *J Inorg Nucl Chem*, 35 (1973) 1127
- 154 P C Uden and D E Henderson, *J Chromatogr*, 99 (1974) 309
- 155 S Dilli and E Patsalides, *J Chromatogr*, 130 (1977) 251
- 156 P J Clark, *Ph D Dissertation*, University of Massachusetts, 1977
- 157 P C Uden, D E Henderson and A Kamalizad, *J Chromatogr Sci*, 12 (1974) 591
- 158 P C Uden and K Blessel, *Inorg Chem*, 12 (1973) 352
- 159 R Belcher, A Khalique and W I Stephen, *Anal Chim Acta*, 100 (1978) 503
- 160 W I Stephen, *Proc Soc Anal Chem*, 9 (1972) 137
- 161 S Dilli and A M Maitra, *J Chromatogr*, 254 (1983) 133
- 162 S Dilli and E Patsalides, *J Chromatogr*, 134 (1977) 477
- 163 S Dilli, A M Maitra and E Patsalides, *Inorg Chem*, 21 (1982) 2832
- 164 E Patsalides, B J Stevenson and S Dilli, *J Chromatogr*, 173 (1979) 321
- 165 L N Bazhenova, K I Pashkevich, V E Kirchenko and A Ya Alztkovich, *Zh Anal Khim*, 36 (1981) 410
- 166 G D Thorn and R A Ludwig, *The Dithiocarbamates and Related Compounds*, Elsevier, Amsterdam, 1962
- 167 J Krupčík, J Garaj, S Holotík, D Oktavec and M Košík, *J Chromatogr*, 112 (1975) 189
- 168 J Masaryk, J Krupčík, J Garaj and M Košík, *J Chromatogr*, 115 (1975) 256
- 169 T J Cardwell, D J DeSarro and P C Uden, *Anal Chim Acta*, 85 (1976) 415
- 170 A Radecki, J Halkiewicz, J Grzybowski and H Lamparaczyk, *J Chromatogr*, 151 (1978) 259
- 171 A Radecki and J Halkiewicz, *J Chromatogr*, 187 (1980) 363
- 172 M L Riekkola, *Finn Chem Lett*, 3 (1980) 83
- 173 M L Riekkola, O Makitie and M Sundberg, *Kem Hemi*, 6 (1979) 525
- 174 R A Zabarova, G N Bortnikov, F A Gorina and K M Samarin, *Zavod Lab*, 47(3) (1981) 22
- 175 J Chovancova, J Krupčík, V Rattay and J Garaj, *J Chromatogr*, 256 (1983) 465
- 176 A Tavlaridis and R Neeb, *Z Anal Chem*, 282 (1976) 17
- 177 A Tavlaridis and R Neeb, *Z Anal Chem*, 292 (1978) 199
- 178 G Hartmetz, G Scollany, H Meierer, A Meyer and R Neeb, *Fresenius' Z Anal Chem*, 313 (1982) 309
- 179 A Meyer and R Neeb, *Fresenius Z Anal Chem*, 313 (1982) 221
- 180 L Sucre and W Jennings, *Anal Lett*, 13(A6) (1980) 497
- 181 T J Cardwell and P S McDonagh, *Inorg Nucl Chem Lett*, 10 (1974) 283
- 182 A Kleinmann and R Neeb, *Z Anal Chem*, 285 (1977) 107
- 183 B Feigler, V Gemmer-Colos, A Dencks and R Neeb, *Talanta*, 26 (1979) 761
- 184 P J Marriott and T J Cardwell, *J Chromatogr*, 234 (1982) 157
- 185 N M Karayannis and A H Corwin, *J Chromatogr*, 47 (1970) 247
- 186 P J Marriott, J P Gill and G Eglinton, *J Chromatogr*, 236 (1982) 395
- 187 P J Marriott and G Eglinton, *J Chromatogr*, 249 (1982) 311
- 188 J C Van Loon, *Anal Chem*, 51 (1979) 1139A
- 189 B Kolb, G Kemmner, F H Schleser and E Wideking, *Fresenius' Z Anal Chem*, 221 (1966) 166
- 190 F M Zado and R S Juvet, Jr *Anal Chem*, 38 (1966) 569
- 191 A J McCormack, S C Tong and W D Cooke, *Anal Chem*, 37 (1965) 1470
- 192 C A Bache and D J Lisk, *Anal Chem*, 39 (1967) 786
- 193 Y Talmi, *Anal Chim Acta*, 74 (1975) 107
- 194 H Kawaguchi, T Sakamoto and A Mizuike, *Talanta*, 20 (1973) 321
- 195 R M Dagnell, T S West and P Whitehead, *Analyst (London)*, 98 (1973) 432
- 196 W R McLean, D L Stanton and G E Penketh, *Analyst (London)*, 98 (1973) 432
- 197 P C Uden, *Dev At Plasma Spectrochem Anal Proc Winter Conf*, 1980, p 302
- 198 R J Lloyd, R M Barnes, P C Uden and W G Elhott, *Anal Chem*, 50 (1978) 2025
- 199 D L Windsor and M B Denton, *J Chromatogr Sci*, 17 (1979) 492
- 200 D Sommer and K Ohls, *Fresenius' Z Anal Chem*, 295 (1979) 337