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REVIEW

Chromatography of organic derivatives of Group IVB elements

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Chromatographic aspects of the analysis of Group IV organometallic derivatives are reviewed. The emphasis is towards gas and liquid chromatography.

Keywords: Gas chromatography, liquid chromatography, Group IV, detectors, separation

CONTENTS

1 INTRODUCTION

Interest in the possibilities of chromatographic analysis of organic derivatives containing Group IVB elements arose almost simultaneously with the development of the corresponding research equipment. A review article of 1970 already cites nine papers on the problem,[1] dating back to 1960–1965. A detailed review dealing with the gas chromatography of organosilicon compounds appeared in 1979.[2] A monograph[3] published in 1982 recorded more than 300 pages devoted to applications of the chromatographic analysis of organoelement compounds containing Group IVB elements, including 165 pages that dealt with organosilicon compounds.

Achievements in the gas chromatography of organoelement compounds are summarized in Ref. 4, but the scope of this review did not allow discussion of the analysis of all Group IVB derivatives in detail.

The present work reviews literature on organosilicon compounds published in 1978–1987, the references listed in Refs 1–4 being given only as necessary. Literature on chromatographic investigations of germanium-containing derivatives and their heavier analogues is discussed as well.

So far, there are more than 1500 publications dedicated to the chromatography of trimethylsilyl and other derivatives of polar organic compounds. Investigations along these lines seldom deal with the specific features of organoelement compounds, the main emphasis being laid on the solution of particular analytical problems of organic and bio-organic chemistry. For this reason many compounds are beyond the scope of this article.

2 ANALYSIS OF DERIVATIVES CONTAINING GROUP IVB ELEMENTS

2.1 Gas chromatography (GLC)

The chromatography of compounds containing different Group IVB elements has been developing unevenly. Thus, the first chromatographic studies on germanium- and silicon-containing compounds appeared in the years 1960–1962.[5] However, recently the number of major works on silicon- and particularly germanium-containing derivatives has

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decreased significantly. On the contrary, beginning in 1978 there has been an upsurge of activities in the field of GLC and HPLC of lead- and tin-containing derivatives.

Scrupulous and systematic chromatographic analysis of alkylhalosilanes, alkylsilanes, and alkoxysilanes used as intermediates in the synthesis of polysiloxanes was due to the development of organosilicon chemistry and chemical engineering. It is important too that many stationary phases used in modern GLC belong to compounds of this class. References 6 and 7 provide typical examples of the successful use of GLC (on packed and capillary columns), TLC and HPLC for the analysis of reaction mixtures of β-trimethylsilyldivinylketones.

At present, organotin compounds are widely used for polymer stabilization,[8] as catalysts, pesticides,[9] and timber preservatives[10] as well as for components of agricultural chemicals and antifouling paint materials.[11]

This largely accounts for the presence of these compounds and their highly toxic decomposition products in natural waters, industrial waste products and foodstuffs.[12] Organotin compounds have been detected in the environment in amounts equal to 10^{-6}–10^{-9} g dm^{-3},[9] explaining the constant interest in the chromatographic analysis of this class of compounds.[13–16]

For example, it has been noted in some publications[17,18] that halo-organotin compounds, especially trichlorostannanes, undergo disproportionation or exchange alkyl radicals under GLC conditions. In order to avoid this, it has been proposed[19] to substitute the halogen atoms for organic radicals, which are normally absent in the test compounds, by reactions with the corresponding Grignard reagent. It has been proposed, too, to convert these compounds into dithiocarbamates prior to chromatography.[20] Disproportionation does not take place under HPLC conditions.[18]

The wide applicability of tetraethyllead as an antiknock agent in petrol and the high toxicity of lead derivatives determines the strategy of research in the chromatography of organolead compounds. From data summarized in monograph[21] it can be seen that very short columns (0.3–0.7 m) are frequently used for analysis of volatile compounds containing lead and tin. This apparently allows minimization of the residence time of thermolabile compounds in the column, especially when there is no need for complete separation (e.g. in the case of group analysis) and can also depend on the specific properties of the highly selective (e.g. element-specific) detectors used (see below). For instance, it is not necessary to separate organoelement compounds from hydrocarbons undetectable by element-specific methods.

Most publications on the chromatographic analysis of organo-lead and -tin compounds are somewhat methodological in character. There may be less attention given to the chromatographic analysis itself. Emphasis is sometimes laid on the preparation of samples, and the preliminary concentration and treatment of biological materials, air and water samples, and bottom deposits. The problems of the actual detection of these compounds are of great interest also.

The solution of some analytical tasks with the aid of gas chromatography is illustrated in Table 1.

2.2 Liquid Chromatography (LC)

To date, the number of publications on the liquid chromatography (LC) of non-polymeric derivatives containing Group IVB elements does not yet appear to have reached 100 papers. This figure seems very small in comparison with the number of papers dedicated to the LC of organic compounds — about 100 publications on the subject appear every week. Most of the former deal with methodological aspects of organo-tin and -lead compound determination in industrial products, in the environment and in biological samples.[111–115]

Sterically hindered 2,4,6-substituted phenols carrying a $Si(CH_3)_3$ or $Ge(CH_3)$ substituent have been investigated under HPLC conditions.[116] Differences in the chromatographic behaviour between compounds of this type and their carbon analogues on silica gel were discussed. The behaviour of silicon-, germanium-, and tin-containing peroxides analysed by liquid partition chromatography is described in Ref. 117. In contrast to other studies, the experimental conditions were widely varied, including:

(a) different types of solid silica gel sorbents used (KSK-2, Silochrom 80, C-3);
(b) different stationary phases (Squalane, Carbowax 600, hydroxydipropionitrile); and
(c) temperature programming.

The preferable use of cyanoalkylated silica gels in some publications[118–120] is based on the fact that

Table 1 Analysis of organoelement compounds containing Group IVB elements by GLC

No.	Compounds under study	Analytical task	Chromatography conditions	Ref.
1	Volatile silanes and germanes	Separation and analysis	DC-702 on Celite 545	5
2	Silanes up to Si_7H_{16}	Analysis of materials for semiconductors	Porapak P; temperature programming: 4 min at 36°C; from 36 to 210°C, 15°C min^{-1}; 20 min at 210°C	22
3	$(Me_2Si)_6$	Study of polycyclization of dimethyldichlorosilane		23
4	Alkyl-silanes and -germanes	Attempted use of complex nickel compounds as stationary phase		24
5	Alkyl-silanes and -germanes	Measurements of retention parameters	3,6,10,13% Squalane, 10% DC-702 on Embacel	25
6	β-Silyl-substituted divinyl ketones	Control of Nazarov-type reaction	11% QF-1 on Chromosorb, capillary column OV-101	6, 7
7	Organosilicon amines	Identification without reference substances	Apiezon L, SE-30, XE-60, CW-20M	26
8	Organosilicon amines	Study of chromatographic behaviour	15% Apiezon L, 5% SE-30, 5% XE-60 on Inerton NAWHMDS at 200°C	27
9	Methyl- and ethyl-chlorosilanes	Comparison of MS and FID sensitivity	Capillary column OV-101	28
10	Chloromethyl and methyl chloro-silanes and -germanes	Analysis of impurities	15% Squalane, on Chromaton N; temperature programming: from 75 to 125°C, 6°C min	29
11	Chloroalkyltrichloro-silanes and -germanes	Analysis of reaction mixtures	15% PFMS, 3% FS on firebrick	30
12	Trimethylalkyl- and alkoxy-silanes	Analysis of semiproducts	Apiezon L, SE-30, Reoplex 400, CW-1500 on Chezasorb; 100°C	31
13	Mixed alkylalkoxysilanes	Determination of retention indices, their additive calculation	Apiezon M, XE-60; 160°C	32
14	Tetraethoxysilane	Thermal decomposition kinetics	5% SE-30 on Chromaton N	33
15	Deuterated cyclosilanes, Vinyltriethoxysilanes	Study of deuteration reaction	CW-20 M on Chromaton N	34
16	Alkylalkoxysilanes	Determination of retention indices, identification	Capillary column OV-1; temperature programming: 50°C to 320°C by 15°C min	35
17	1-Methyl-3,7,10-tris(trifluoro-propyl)silatrane	Preparative isolation of diastereomers	E-301, 150°C	36
18	$[(CH_3)_2SiO]_n$; $n=40$, mol.wt lup to 3000	Separation of oligomers	9% spec. polymer Dow Corning on Chromosorb WAW; temperature programming; 50–390°C	37
19	Methyl- and methyl(2-thienyl)-siloxanes and cyclosiloxanes	Determination of volatile components in siloxane liquid PMTS-1	5% SE-30 on Chromaton N: temperature programming	38
20	Methylphenyl- and methylthienyl-oligo-cyclosiloxanes	Study of isomeric composition	PFMS-4, PFMS-6, FS-303; temperature programming: 50–300°C	39
21	Nitrogen-containing siloxanes and silazanes	Analysis of synthetic semiproducts	Apiezon L, SE-30, PFMS-4 on Chezasorb; 170–270°C	40
22	Methylethyloctasil-sesquioxanes	Analysis of products obtained in the reaction of ethylpolycyclosiloxanes with methyltrichlorosilane	3% OV-17 on Chromosorb W; temperature programming: 120–210°C by 4°C min^{-1}	41
23	Siloxanes and silazanes	Identification without reference substances	Apiezon L, SE-30, Reoplex-400, CW-20 M	42

Continued

Table 1 (continued)

No.	Compounds under study	Analytical task	Chromatography conditions	Ref.
24	Oligomers of methyl- and methylvinyl-siloxanes	Identification without reference substances	Capillary column, OV-101	43
25	Methylsilgermoxanes	Quantitative determination	PE-A; 150°C	44
26	Alkyl- and phenyl-silazanes and -siloxanes	Identification without reference substances	Apiezon L, SE-30, PMS-100	45
27	Cyclosilazanes and cyclosilazocanes	Identification without reference substances	Apiezon L, SE-30, CW-20 M, XE-60	46
28	Alkoxy-silanes and -germanes	Quantitative and qualitative analysis of mixtures	1% Apiezon L on Chromosorb W; temperature programming: 60–150°C by 15°C min^{-1}	47
29	$(CH_3)_4M$; M = Si, Ge, Sn, Pb	Determination of retention parameters	Apiezon L	48
30	Ethyl-silanes, -germanes, -stannanes	Determination of thermodynamic functions of sorption; identification	20% Apiezon L, 15% CW-20 M on Chromosorb G; 100°C, 130°C	49
31	Silicon, germanium and organostannic compounds	Determination of thermodynamic functions of sorption; identification	2% Apiezon L, 5% DEGS on Chromosorb G; 100°C, 200°C	50
32	$(C_4H_9)_4Ge$ and $(C_4H_9)_4Sn$	Determination of trace amounts	5% CW-20 M on Chromosorb W	51 52
33	Alkyl-silanes, -germanes, -stannanes and -plumbanes	Study of the rearrangement products in Friedel–Crafts reactions	5% OV-101 on Chromosorb 750, 3% OV-101 on Ultrabond 20 M, capillary column OV-225 (SCOT)	
34	Mixed hexa-alkyldigermanes	Determination of isomeric composition	3% Squalane, 3% DC-702 on Embacel	53
35	Alkylsilanes, urono-, di-, tri- and tetra-alkylgermanes	Comparison of retention parameters with hydrocarbon analogues	2–13% Squalane on Embacel; 100°C	54
36	$Ge_n(CH_3)_{2n+2}$; $n = 3–5$	Determination of retention parameters with high accuracy	Nitrotoluene, XF-1112, QF-1 SE-30, Apiezon L on Chromosorb W; 30–240°C	55
37	$(C_2H_5)_3M—M'(C_2H_5)_3$; M and M' = Si, Ge, Sn	Determination of thermodynamic functions of sorption; identification	Apiezon L, 200°C, 250°C; CW-20, 150°C, 200°C; graphitized carbon black, 200°C, 250°C	56
38	Unsaturated organosilicon and organogermanium compounds	Separation of *cis-* and *trans-* isomers	20% Apiezon L on Chromosorb W, 160°C; graphitized carbon black, temperature programming: 100–200°C	57
39	Trimethylchlorogermane, hexaethyldisilane, hexaethyldigermane	Preparative isolation	20% UCW-95 on Chromosorb W; temperature programming: 50–200°C by 8°C min^{-1}	58, 59
40	Alkylchloro-germanes and -stannanes	Analysis under extremely inert conditions	20% octadecane on Polychrom -1, Teflon column	60
41	$(C_2H_5)_3GeX$; X = Cl, NCO, OCH_3, $N(C_2H_5)CH_2COOCH_3$	Qualitative and quantitative analysis	20% Apiezon L on Chromosorb W; 196°C	61
42	Fluorine-containing organogermanium compounds	Determination of thermodynamic functions of sorption; identification	20% Apiezon L, 15% Carbowax 20 M, Carbochrom C, Carbochrom C + 0.01% Apiezon L	62
43	Perfluorovinylstannane	Analysis and purification	Paraffin oil	63
44	Different organotin compounds	Determination of retention parameters	Apiezon L, SE-30, 214°C; SKTFT-50, 188°C	64

Continued

Table 1 (continued)

No.	Compounds under study	Analytical task	Chromatography conditions	Ref.
45	Tetramethyl- and tetraethyl-stannanes	Comparison of GLC and HPLC applicability for analysis of trace amounts	3% SE-30 on Chromosorb G AW DMCS; 120°C, 180°C	65
46	Trimethylalkyl-stannanes	Analysis of reaction mixtures		66, 67
47	Tetra-alkylstannanes	Determination of trace amounts	3% OV-101 on Chromosorb WAW; 100°C, 150°C	68
48	Tri- and tetra-alkylstannanes	Determination of retention parameters	20% CW-20 M, 20% E-301, on Chromosorb W; 150°C, 200°C	69
49	Tetramethyl-, tetraethyl- and tetrabutyl-stannanes	Selection of the most inert sorbent	Five different sorbents	70
50	Triphenylstannanes	Study of decomposition in water	10% DC-200, 3% OV-17 on GasChrom Q; 110°C	71
51	$(C_4H_9)_nSn(C_5H_{11})_{4-n}$	Detection of trace amounts		
52	Alkylalkenylstannanes	Comparison of different detection methods	3% SE-30 on Super Pak 20M	72
53	$(CH_3)_3SnR$, $R = CH_3$, Cl, C_2H_5, C_2H_5, $Sn(CH_3)_3$	Identification of $(CH_3)_4Sn$ impurities	5% SE-30, 15% CW-1500 on Chromaton NAWDMCS; 70°C	73
54	Butylstannanes	Determination of Bu_3Sn^+ trace amounts in water		74
55	Tetramethyl- and tetraethyl-stannanes and -plumbanes	Estimation of atom-fluorescence spectrometer as detector	Capillary column	75
56	Tributylstannanes and triphenylstannane	Identification in biological samples and bottom deposits	20% CW-20 M, 2-104, OV-1, 3% SE-30, 2% OV-17, 15% DEGS, OV-225; 60°C, 150°C	76
57	Di- and tri-butylstannanes	Determination in seawater	1,5% OV-101 on Chromosorb GHP; temperature programming: 23–107°C, by 32°C min^{-1}	77
58	Butylstannanes	Determination in water		78, 79
59	Alkylchlorostannanes	Study of stability under GLC conditions	Silicone elastomer 7100, MFSD-3 on Chromosorb or Celite 545	17
60	Methylchlorostannanes	Environmental control	5% OV-101, 5% OV-17 on Chromosorb WHP; 52°C, 55°C	80
61	Methylchlorostannanes	Determination in bottom deposits	0.2% CW-1500 on Carbopak C; temperature programming: 40–120°C by 15°C min^{-1}, 120–150°C by 30°C min^{-1}	81
62	Alkylhalostannanes	Study of GLC and HPLC applicability		18
63	Trialkylchlorostannanes, tetra-alkylstannanes	Identification in biological samples	20% DEGS in Chromosorb W, 10% CW-20 M on Shimalite W; temperature programming: 50–150°C by 4°C min^{-1}	82, 83
64	Butylchlorostannanes	Analysis of reaction mixtures	18% Silicone OE-4011 on Sterchamol; 180°C	84
65	Butylhalostannanes	Analysis of industrial wood preservatives	4% SE-30 on Chromosorb W; 160°C	10
66	$(C_4H_9)_nSnCl_{4-n}$	Derivatization to *N,N*-dialkyldithiocarbamates, procedure optimization	3% OV-101 on Chromatone N-Super	20
67	$C_4H_9SnCl_3$	Determination in seawater	Capillary column DB-5	85
68	Butylbromostannanes	Analysis of $(C_4H_9)_2SnBr_2$ radiation-chemical synthesis products	High-vacuum silicone grease on Chromosorb W; temperature programming: 50–200°C by 25°C min^{-1}	86
69	$HexBu_2SnCl$	Environmental control	Capillary column Pluronic L64, PS-255	87
70	Butyl-, octyl- and phenyl-bromostannanes	Quantitative analysis	5% Silicone MS-200 on Celite 545; 110°C, 180°C, 210°C	88

Continued

Table 1 (continued)

No.	Compounds under study	Analytical task	Chromatography conditions	Ref.
71	Alkylbromostannanes	Selection of optimal stationary phase and separation	CW-20 M, SE-30, QF-1, SKTFT-50, on Chromosorb W, Chromosorb G, Polychrom-1	89
72	Alkyl- and phenyl-halostannanes	Development of Grignard derivatization method		19
73	$(Bu_3Sn)_2O$	Determination in marine products, development of preparative method	10% Terman-Hg	90
74	$(CH_3)_nPb(C_2H_5)_{4-n}$	Determination in petrol gasoline	Ultra-bond 20M; temperature programming: 30–120°C	91
75	$(CH_3)_nPb(C_2H_5)_{4-n}$	Determination in petrol gasoline		92
76	$(CH_3)_nPb(C_2H_5)_{4-n}$	Determination in petrol gasoline	20% Apiezon M on Chromosorb; 70°C	93
77	$(CH_3)_nPb(C_2H_5)_{4-n}$	Determination in petrol gasoline	20% CW; 70°C	94
78	$(CH_3)_nPb(C_2H_5)_{4-n}$	Determination in petrol gasoline	20% Cyanethoxypropane on Chromosorb P, 80°C	95
79	$(CH_3)_nPb(C_2H_5)_{4-n}$	Determination in atmosphere	3% OV-101 on Chromosorb W; 80°C	96
80	$(CH_3)_nPb(C_2H_5)_{4-n}$	Determination in water, bottom deposits and fish	Capillary column	97
81	$(CH_3)_nPb(C_2H_5)_{4-n}$	Selectin of optimal conditions for separation and detection	3% OV-101 on Gas Chrom Q	98
82	$(CH_3)_nPb(C_2H_5)_{4-n}$	Determination in atmosphere	3% OV-101 on Gas Chrom Q	99
83	$(CH_3)_nPb(C_2H_5)_{4-n}$	Determination in atmosphere	10% CW-20M	100
84	$(CH_3)_nPb(C_2H_5)_{4-n}$	Determination in water	10% SE-52 on Chromosorb W AW DMCS; 60°C	101
85	Tetraethyllead	Determination in water	10% SE-52 on Chromosorb P; 80°C	102
86	Tetraethyllead	Analysis of industrial solutions	15% Reoplex 400, 15% CW-4000 on Chromosorb W AW DMCS; 75°C	103
87	Tetra-alkylplumbanes	Determination in water	10% OV-1 on Chromosorb W; temperature programming: 80–200°C by 5°C min^{-1}	104
88	Tetraethyllead	Comparison of GLC and AA spectroscopy		105
89	Tetraethyllead	Determination in gasoline		106
90	Alkylplumbanes up to Bu_4Pb	Developments of derivatization procedure and determfination in water	10% OV-101 on Chromosorb; temperature programming: 80–180°C by 20°C min^{-1}	108
91	Alkylplumbanes up to Bu_4Pb	Determination in gasoline		108
92	Trialkylchloro-plumbane	Determination trace amounts	10% OV-101 on Gas Chrom Q	109
93	Trialkylchloro-plumbane	Determination in industrial wastes	SP-2100, capillary column; temperature programming: 70–270°C by 20°C min^{-1}	110

chlorine-containing organotin compounds are highly polar. This impedes the use of silica gel. On the other hand, reversed-phase chromatography cannot be used because of the hydrolytic instability of many solutes in aqueous mobile phases.

The behaviour of compounds having the general formula Sn_nR_{2n+2}, where $n = 2–5$, R = n-C_4H_9, i-C_4H_9, n-C_8H_{17}, under conditions of reversed-phase chromatography on octadecylsilica was studied.[121] Methanol or its mixture with 2-propanol (30/70 v/v) were used as eluents. The equation proposed to describe the retention pattern of these compounds takes into account the number of tin atoms in the molecule (Eqn [1]):

$$\ln k' = a_0 + a_1 n_{Sn} \qquad [1]$$

where k' is a capacity factor; n_{Sn} is the number of tin atoms per molecule; a_0, a_1 are coefficients.

This relationship was used for the identification of compounds that had not been studied earlier. Preparative separation of some alkylstannanes was described.

Reference 122 reports the separation of diastereomers of 3,7,10-trimethyl-substituted 1-(4′-tolyl)silatranes under HPLC conditions.

The application of different types of columns for the separation of methyltin chlorides is described in Ref. 123. Binary and ternary eluent have been used for the separation of compounds containing a $(C_4H_9)_3SnO$— radical by reversed-phase chromatography (RPC).[124] Direct separation of optical isomers was achieved for compounds of general formula $R^1R^2R^3R^4M$ (R^1 = CH_3, C_2H_5; R^2 = $(CH_3)_2CH$, $C_6H_5CH_2$, $C_6H_5(CH_3)_2CCH_2$; R^3 = C_6H_5, $C_6H_5CH_2$; R^4 = C_6H_5, $(C_6H_5)_3C$ in the case of M = Sn and R^4 = H, Cl in the case of M = Ge). Though column efficiency did not permit a complete separation of the isomers, the specific rotation measurements for the fractions collected (λ = 365 nm) showed partial separation in all cases. It must be noted that in the case of tin it was the laevorotatory isomer that was eluted first, while in the case of germanium it was the dextrorotatory isomer.[159,160]

One- and two-dimensional thin-layer chromatography (TLC)[125] has been frequently applied for the separation of various organotin compounds[125–127] and for total analysis of sulphur-containing organotin compounds.[128] The thin-layer chromatography of silatranes is described in a Czechoslovak patent.[129] The procedure involved the conversion of organyltrialkoxysilanes into silatranes by the reaction with triethanolamine in the presence of alkali. However, because of the failure to identify trans-annular bonds in these compounds, the reaction products were formally called bicyclic.

In the lead organics area, HPLC as well as GLC was most often used for the analysis of tetraethyllead and related compounds. Reversed-phase chromatography on sorbents with various alkyl chain lengths has been generally used for their analysis.[130–132]

Arylacetoxy-plumbanes have been studied in detail by thin-layer chromatography on silica gel. The R_f values for a large number of individual and mixed eluents are summarized in Ref. 133. The separation of organolead halides and the mechanism of tetraethyllead decomposition in seawater are described in Ref. 134.

3 DETECTION OF ORGANOELEMENT COMPOUNDS

Gas chromatographic detection of organosilicon compounds is extensively treated in Ref. 2. The characteristics, applications and limitations of flame-ionization detectors (FID) and thermal conductivity detectors (TCD, catharometers) are discussed along with less frequently used equipment. Practically all known detector types for gas and liquid chromatography have been used for analysis of organoelement compounds. There is a paper reporting the scanning of TLC plates using an ionizing radiation counter for detection of ^{14}C-labelled compounds.[125] Optimization of selective methods for detection of organolead and organotin compounds is under way.

It is worth noting that flame ionization detectors with hydrogen atmosphere (HFID) (see for example Refs 72, 91) and a specially designed luminiscent detector[51] resulted from gas chromatographic investigations on organoelement compounds containing Group IVB elements. The luminescent detector described in Ref. 51 satisfies the most stringent selectivity and sensitivity requirements.

Using the surface luminescence mode, 0.2 pg of organotin compounds could be detected, but using a specially designed apparatus 0.04 pg or 5×10^{-16} g Sn s^{-1} could be measured.

Recently, atomic-absorption (AA) and flame-emission detectors (FED) have been widely used for the detection of organoelemental compounds by GLC and HPLC.[29,77,101,105,107,135,136,161,162] In some cases, precolumn derivatization was proposed for improving the detection parameters.[77,101,137] Problems involved in the design of interfaces between chromatograph and spectrometer are treated in detail in Refs 65 and 138.

Electrochemical detection of alkyl derivatives of lead in the system acetonitrile–0.05 mol dn^{-3} Et_4NC10_4 — mercury dropping electrode is described in Ref. 129. It has been noted[39,140] that FID can be very easily overloaded by organosilicon compounds. This results in decreased detection linearity. Peak inversion can be observed[141] with the formation of two anomalously

Table 2 Characteristics of detectors applied in the chromatography of derivatives containing Group IVB elements

Detector[a]	Method	Element	Sensitivity (ng per injection)	Comments	Ref.
TCD	GLC	Si	10000–200000		65
FID	GLC	Si	50		28
		Sn	10–100	80	
		Pb	5–25	109	
NPD	GLC	Si	50	Addition of CH_4 in carrier gas	142
HFID	GLC	Sn	10	Selectivity relative to hydracarbons 1:1000, addition of SiH_4 to hydrogen	72
		Pb	0.5		91
EC	GLC	Sn	0.02		82, 83
FPD	GLC	Sn	0.1		9
		Pb	0.5	λ = 406 nm	143
MS	GLC	Si	7		28
Luminescent	GLC	Ge	0.001	λ = 600–650 nm	51
		Sn	0.0002	λ_{max} = 390 nm	51
IR spectrometer	GLC	Sn			66
Flame emission spectrometer	GLC	Pb	0.005		110
		Si			110
		Ge			52
		Sn	0.02	Selectivity relative to hydrocarbons 1 : 1000–880000	52
		Pb			52
	HPLC	Pb	25		111
AA spectrometer	GLC	Sn	1	Electrothermal ionization	65
		Sn	3	Electrothermal ionization with hydrogen addition	
	HPLC	Sn			130,144
		Pb	$(10–15) \times 10^{-1}$	Flame ionization	137
		Sn		Electrothermal ionization with the addition of hydrogen	65
Refractometer	HPLC	Sn	50000		65
UV photometer	HPLC	Pb	0.1	λ = 254 nm	130
	HPLC	Pb	100	Derivatization, λ 546 nm	131
Fluorimeter	HPLC	Sn	20	Derivatization, λ = 420 nm, λ_A = 500 nm	118–120
Examination of plates under UV radiation	TLC	Pb	10		134

[a] Abbreviations: TCD, thermal conductivity detectors; FID, flame ionization detection; NPD, nitrogen–phosphorus detector FID; HFID, hydrogen atmosphere FID; EC, electron capture; FPD, flame photometric detection; MS, mass spectrometry; IR, infrared; AA, atomic absorption; UV, ultraviolet.

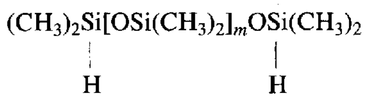
narrow peaks on the chromatogram of an individual compound. This effect depends on the percentage of silicon in the compound studied.[140] Characteristics of some detection systems are listed in Table 2.

4 SORPTION REGULARITIES

The carbon skeleton structure and the presence of Group IVB elements in organoelement compounds are largely responsible for their chromatographic behaviour. Organoelement compounds display all the principal features typical for carbon derivatives. Thus, retention parameters of a wide range of organosilicon compounds are correlated with their molecular weight, the number of carbon atoms in the molecule, Taft's induction constants, etc.[26,31,40,45,46] The retention parameters of organo-silicon, -germanium and -tin compounds are related to thermodynamic functions of sorption and solubility.[49,50,56,57,62]

Apart from these common characteristics there are other parameters depending on the presence of silicon or its analogues in the molecule. The retention model proposed in Ref. 31 suggests that the positively charged silicon atom in alkylalkoxysilanes (due to the negative inductive effect of the OAlk group) interacts directly with the active site of the polyester stationary phase. In fact, successive substitution of alkoxy groups for alkyl groups results in a decreased ΔI value, suggesting a weakening of specific interactions with the stationary phase. (ΔI is a difference between Kovats (or retention) indices (I) on polar and non-polar liquid phases.) In our view, even a methyl group effectively shields the silicon atom, making it practically inaccessible to intermolecular interaction. This effect is more likely due to the interaction of oxygen atoms with the corresponding stationary-phase (SP) groups.

The chromatographic behaviour of oligodimethylsiloxanes of general formula



$$(CH_3)_2\underset{|\atop H}{Si}[OSi(CH_3)_2]_mO\underset{|\atop H}{Si}(CH_3)_2$$

(including compounds with $m = 11$, e.g. having a molecular weight of about 1000) can be described by Eqn [2]:

$$\ln V_g = a_0 + a_1 n_{Si} \qquad [2]$$

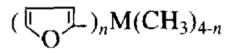
where V_g represents specific retention volume, n_{Si} is the number of silicon atoms in the molecule, and a_0 and a_1 are coefficients.

A large body of experimental data has been accumulated on the chromatographic properties of germanium derivatives.[25,53,54] The behaviour of solutes under study was expressed by retentions relative to mesitylene. The specific retention volume of this standard solute was assumed to be 100. A linear dependence on the number of germanium atoms in the molecule and on the number of carbon atoms in the homologous series of mono-, di- and tri-germanes was established for different mixed alkylgermanes Ge_nR_{2n+2}, where $n = 1-4$. Increments per GeR_2 group were estimated as equal to $\frac{1}{4}\ln V_g$ for the corresponding symmetrical tetraalkylgermanes. These increments were calculated.

A reasonably good prediction value of the proposed models was noted. Retention data were compared with the behaviour of carbon analogues and their boiling points. The longer the alkyl radical, the better was the prediction of retention time. This probably is a manifestation of the general rule that linear models have decreased precision for the first members of the homologous series.

Equation [2] for volatile alkylgermanes and silanes on squalane is described in Ref. 24. As in other cases, the model is only applicable to limited groups of structurally related compounds. Experimental data[145] lead us to conclude that α,ω-dihydro-oligomethylsiloxanes are preferably retained by structurally similar stationary phases (SE-30, PMS-100).

The retention indices (I) of 2-furyl derivatives of general formula[146]



where M = Si, Ge, Sn, Pb; $n = 1-4$, can be related to their structure by Eqns [3] and [4].

$$I = a_0 = a_1X_1 + a_2n \qquad [3]$$

$$\Delta I = b_0 + b_1X_1 + b_2n \qquad [4]$$

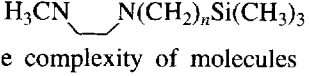
where X_1 stands for the atomic weight of element M and I is the retention index. The values X_1 and n are mutually independent, and coefficients a_2 and b_1 depend on the character of solute interaction with the corresponding stationary phase (SP). Coefficients in Eqn [4] can be calculated not only by statistical treatment of experimental data but also by using term-by-term subtraction of coefficients in Eqn [3] for the corresponding SP pair. The b_2n term is mainly responsible for the polar interactions; b_1X_1 does so to a considerably lesser degree probably due to the efficient shielding of element M.

The non-additivity of structural fragment contributions to the retention of methyl- and ethyl-polycyclosiloxanes is described in Ref. 147. In this case the dependence of I on the number of monomeric units in the oligomer (n) can be expressed by Eqn [5]:

$$I = a_0 + a_1\sqrt{n} + a_2n \qquad [5]$$

The relationship between CH_2 group increments in tetra-alkylsilanes and the charge sign on the terminal carbon atom is reported in Ref. 148; β- and γ-CH_2 group increments differ twofold (on the basis of this evidence an attempt has been made to explain the anomalously low I values of tetramethylsilane). It has been assumed that the negatively charged outer part of the molecule prevents them from dissolution in the stationary phase.

Anomalously low I values, especially on polar stationary phases, have also been observed for compounds of the general formula[149]



although the complexity of molecules and possible shielding of nitrogen atoms did not permit a definite conclusion as to the involvement of the silicon atom in this phenomenon.

The inductive effects of substituents on the retention of 1-(trimethylsilylalkyl)-pyrrolidines, -piperidines and -perhydroazepines on stationary phases of varying polarity have been studied.[150,151] Increments of CH_2 groups in the trimethylsilylalkyl radical are invariably close to 100 units of I. A higher polarity of organosilicon compounds, as compared with their carbon analogues, is characteristic of all these compounds. It has been found too that differences in the basicity of these compounds do not affect appreciably the values of retention parameters.

A fairly rare phenomenon — a negative ΔI value calculated as a difference in I values on QF-1 and SE-30 — has been observed for the first time.[55] Later, similar results were obtained[38] for linear oligomethylsiloxanes and for cyclic siloxanes and silazoxanes.[46] In the latter study the ΔI values for the stationary-phase pair of XE-60 and SE-60 amount to -120 units. Formally, this fact can be regarded as an indication that polydimethylsiloxane SE-30 acts as a more polar stationary phase than nitrilsiloxane XE-60, which is impossible to assume on the basis of McReynolds constants for these stationary phases. This phenomenon could be explained by the close structural similarity of the analysed compounds and the stationary-phase SE-30.[46] This explanation however does not seem sufficient because, in effect, it virtually repeats the ancient principle that 'like dissolves like'. Without questioning the validity of this general principle, it must be pointed out that the problem lies in a considerably weaker solubility of n-alkanes in siloxanes used as stationary phases. As it follows from the experimental findings, the negative ΔI values would not be obtained at all if, for example, Apiezon L had been selected as a non-polar stationary phase for ΔI calculations.

High-performance ion-exchange chromatography (HPIEC) has been applied to investigate the dependence of retention on the type of electrolyte used (CH_3COONH_4, $NaNO_3$, NH_4NO_3).[152] A capacity factor (k') can be described as follows (Eqn [6]):

$$k' = a_0 + a_1\left(\frac{1}{\mu}\right) \qquad [6]$$

$$r = 0.900\text{–}0.955$$

when μ is the ionic strength of the eluent solution, a_0 and a_1 are coefficients, and r is the correlation coefficient.

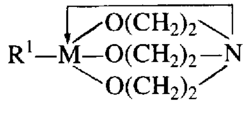
The relationship between retention and the structure of solutes is expressed as Eqn [7]:

$$\ln k' = a_0 + a_1\sigma^*_R \qquad [7]$$
$$r = 0.992$$

where σ^*_R is the Taft's induction constant.

This equation holds true for all classes of compounds except for aryl-substituted ones. It is noted too that if the value σ^* is substituted for the analogous σ^{Ph} value taken from Refs 144 and 153, a good correlation would be observed for the remaining series. Data on the reproducibility of quantitative analysis are also given in this study.

We have investigated the chromatographic behaviour of a large group of atranes of general formula



$$R^1\text{—}M(\text{—}O(CH_2)_2\text{—})_3N$$

where M = B, Si, Ge, Sn using GLC, HPLC and TLC. Compounds of this type and related structures containing a five-coordinate (four in the case of B) element atom[154–156] possess anomalously high retention parameters that cannot be predicted by formal examination of their structures. For example, the ΔI value for 1-phenoxysilatrane on OV-225 amounts to more than 1500 units. It has been demonstrated that the effect of substituent R^1 can be taken into account by using a modified Taft's equation (Eqn [8]):[155]

$$I + a_0 + a_1 n_c + a_2\sigma^* + a_3E^0_s \qquad [8]$$

where n is the number of carbon atoms in R^1, σ^* is Taft's induction constant and E^0_s is a steric constant for R^1.

The character of the complex-forming element, the atrane skeleton structure and substituents at the element atom are responsible for the retention of atranes in GLC. The anomalously high values of retention parameters are due to increased steric accessibility of the oxygen atoms of five- and six-membered cyclic structures in the atrane skeleton.[157]

The effect of substituents on atrane retention in TLC resembles their effect on retention parameters in gas chromatography.[158] It has been shown too that atranes follow all basic retention regularities that are typical of the HPLC process.

The parameters characterizing the effective size of solute molecules and their polarity in gas chromatography can be applied for the evaluation of their behaviour in reversed-phase chromatography.

5 CONCLUSION

Experimental evidence accumulated by GLC of derivatives containing Group IVB elements speaks for a wider application of GLC in chemical investigations. Further development of liquid chromatography methods, optimization and design of commercially available selective detectors, detailed analysis of sorption regularities aimed at providing a theoretical basis for the development of chromatographic separation methods and interpretation of chromatograms are among the main research priorities in the future.

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