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Gas Chromatography of Organometallic Compounds of Groups I-IV of the Periodic System

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The development of the gas-chromatographic analysis of organometallic compounds of groups I-IV of the periodic system in the period 1960-1972 has been reviewed. The characteristic features of the gas-chromatographic analysis of organometallic compounds have been discussed. The use of reaction chromatography for the analysis of the organic compounds of the metals of groups I-IV has been examined. The bibliography contains 238 references.

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I. INTRODUCTION

The present review deals with the gas chromatography of organic compounds of the non-transition metals of groups I-IV. It should be noted that published data on the gas chromatography of the organic compounds of non-transition metals are not evenly distributed. There are almost no papers on the analysis of organic compounds of rubidium, caesium, barium, indium, or thallium, and few papers on the gas chromatography of organometallic compounds of groups I-III, apart from organomercury compounds[1,2]. The problems of the gas-chromatographic analysis of organometallic compounds of group IV have been examined in most detail[3,4].

As far as the analysis of the organic compounds of transition metals is concerned, the gas-chromatographic analysis of the organic compounds of most transition metals is still in the stage of initial development.

II. CHARACTERISTIC FEATURES OF THE GAS-CHROMATOGRAPHIC METHOD FOR THE ANALYSIS OF ORGANOMETALLIC COMPOUNDS

Organometallic compounds are generally highly reactive, many tending to undergo spontaneous ignition or oxidation by oxygen and hydrolysis by water. With the exception of some lower alkyl derivatives, these compounds are solids or liquids with boiling points in the range 200-450°; they are most frequently thermally unstable at temperatures close to the boiling point.

As a consequence of these characteristic features of the physicochemical properties and structure of organometallic compounds, the gas-chromatographic analysis exhibits various specific features.

Stationary phases and carriers. The gas chromatography of organometallic compounds most frequently involves gas-liquid chromatography. Gas-adsorption chromatography has found only limited application[5-7].

The high boiling point of most organometallic compounds makes it necessary to use high-temperature stationary phases, and the increased reactivity of organometallic compounds restricts the choice of materials considerably. Thus of the hundred or so sorbents used for the analysis of organometallic compounds, more than half have silicone stationary phases (the methylsilicones PMS, Se-30, E-301, MS-200, and Gi-7100; the phenylsilicones PFMS, FS, DC-550, DC-702, and OE-4011; the fluorosilicones SKTFT, QF-1, and SF-96, and the nitrylsilicone XF-1112). Much less extensive use is made of strongly polar stationary phases (nitrobenzene and 1,2,3-tris(2-cyanoethoxy)propane), phases of medium polarity (dibutyl phthalate, dinonyl phthalate, diethylene glycol succinate, and butane-1,4-diol succinate), or hydrocarbon phases (Apiezon). In the selection of the stationary phase it is necessary to take account of the possibility of decomposition of the organometallic compounds. In particular, alkyltin hydrides decompose on squalane, chlorosilanes on polyethylene glycol[8], and alkylmercury halides on tricresyl phosphate[9].

As a rule, the separation of organometallic compounds is carried out using sorbents with a low percentage of stationary phase (5-10%); this makes it possible to lower the working temperature and to prevent the thermal decomposition of the compounds being analysed, to decrease the time taken for the analysis, to increase the length of time for which the stationary phase can be used, and to extend the choice of stationary phases.

Organometallic compounds are polar or weakly polar compounds, and the most inert diatomite carriers are used for their analysis (celite 545, Chromosorb W, Silo-cel S-22, modified Inzer brick, and quartz sand (flusine) [sic][9]). The carriers have been modified by treatment with silanes[8] or alkali[10] to decrease their catalytic activity. The use of Fluoroplast carriers is of considerable interest.

Characteristic features of the operation of detectors, and quantitative measurements. The thermal conductivity detector has found the most extensive application in the analysis of organometallic compounds. At high filament temperatures, or when high concentrations of the organometallic compounds are used, however, partial decomposition of the compounds on the incandescent filaments of the catharometer takes place[8]. The metal, which is deposited in a highly dispersed state, and the tarry residues bring about a decrease in sensitivity and an increase in the noise level. In these cases it

is best to use a catharometer with glazed filaments, and to dry the carrier gas thoroughly, in order to avoid the deposition of hydrolysis products in the detector.

A density meter has been used successfully by a number of authors[8,11,12] in the analysis of organometallic compounds. The calibration of a detector of this type is simple.

In early work on the gas chromatography of organic compounds of silicon and tin[13,14], the separated compounds were oxidised to water and carbon dioxide, with subsequent conversion of the water into hydrogen (detected by Green's method[15]).

When a flame-ionisation detector is used, the combustion of the organometallic compounds leads to the formation of the metal oxides, which accumulate on the electrodes; these oxides are insulators, and they alter the electrical characteristics of the detector[8]. A number of authors[8,16] have observed inversion of the peaks of organometallic compounds when a flame-ionisation detector is used. The detection of organosilicon compounds in the form of negative peaks by using a mixture of hydrogen and small quantities of methane as carrier gas has been proposed[16,17]. Organic compounds are then recorded as positive peaks, with a lower sensitivity.

The most reliable results have been obtained using a flame-ionisation detector with both electrodes in the vertical position and a hydrogen burner with a nozzle of small cross-section, since a decrease in the diameter of the nozzle of the burner increases the rate of flow of gas and decreases the proportion of oxidation products[18].

The sensitivity of the flame-ionisation detector towards organometallic compounds is less than its sensitivity towards organic compounds[8,18], and a sharp decrease in sensitivity takes place with increase in the relative proportion of metal in the molecule of the organometallic compound[19]. In spite of the above difficulties, the flame-ionisation detector has been used for the analysis of organic compounds of tin, silicon, lead, and mercury[8,10,18-23].

In the analysis of micro-quantities of organometallic compounds in various media it is possible to use highly-sensitive selective detectors—electron-capture, thermo-ionic, flame-emission, coulometric, and flame-photometric. The electron-capture detector has an increased sensitivity with respect to organomercury and organolead compounds and is often used for their analysis[24-31] including their determination in the biosphere (air[31], water[26,29], and soil[28]). The electron-capture detector has also been used in the analysis of alkyltin and alkylgermanium halides[32]. Traces of organometallic compounds containing halogen atoms have been identified by comparing the signals from thermo-ionic halogen and flame-ionisation detectors[33]. The sensitivity of electron-capture or thermo-ionic detectors is greater than that of flame-ionisation detectors by a factor of several hundreds or even thousands[24].

In the analysis of organosilicon compounds, use has been made of a specific "silicone" detector, based on a combination of flame-emission and atomic-absorption detectors[34].

Different methods of quantitative analysis are used in the analysis of organometallic compounds; the internal-standard method is most frequently employed, and the absolute-calibration method is used less frequently. Wurst[12] has analysed the errors in the quantitative determination of organosilicon compounds. The results are typical of the quantitative analysis of other types of organometallic compound. The mean relative error usually does not exceed 7% if the component is present in quantities of 1–2%. The error is appreciably smaller (3%) at higher concentrations of the component. At very low concentrations of the order of 0.1–0.001%, the mean error reaches 10–12%.[19] In quantitative calculations it is necessary to take account of the possibility of mutual transformations ['scrambling'] of the organometallic compounds being analysed[35].

Methods of introducing the specimens. In the case of reactive organometallic compounds which tend to ignite spontaneously, the specimens are introduced in an inert atmosphere. Fig. 1*A* gives a diagram of the so-called three-needle method for the introduction of specimens[36]. When the nitrogen outlet is closed, the specimen is forced into the syringe.

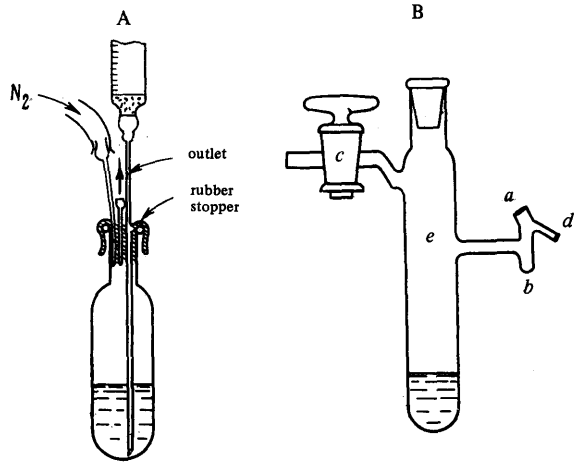


Figure 1. Apparatus for working with unstable liquids.

The specimen can be introduced into the chromatograph[37] directly from the sampler (*e*) (Fig. 1*B*). For this purpose, part of the specimen is poured into the cell (*b*). The needle of the micro-syringe is introduced through the stopper of the tube (*a*) and the syringe is flushed beforehand by passing a stream of dry nitrogen through the tap (*c*). The needle is then lowered into the liquid and the syringe is filled. For the introduction of the specimen into the chromatograph, the needle of the syringe is introduced into the tube (*d*), the end of which is closed by a stopper; when the latter is punctured, the specimen passes to the volatiliser of the chromatograph.

In some cases the introduction of specimens can be carried out by means of syringes previously flushed with an inert gas and carrying on the ends of their needles a self-sealing covering[38].

The drying of the carrier gas is most frequently carried out with phosphorus(V) oxide and molecular sieves. A method for the quantitative determination of the residual moisture in gases after drying has been published[39]. The sensitivity of the determination corresponded to 2×10^{-3} mg water in 1 litre of gas for a volume of specimen being analysed equal to 0.5 ml.

III. RELATIONSHIP BETWEEN THE STRUCTURE AND CHROMATOGRAPHIC BEHAVIOUR OF ORGANOMETALLIC COMPOUNDS

For the identification of organometallic compounds, use is made of the usual relationship between the retention and structure of organic compounds[40-42], but in a number of cases the behaviour of organometallic compounds is so unique that all the correlations must be rigorously verified. Sometimes it is more appropriate to relate the retentions of organometallic compounds not to the retention volumes of the normal paraffins, used as standards, but to the retentions of a series of organometallic homologues.

Wurst[43] put forward modified retention indices I_{Si}, in which the retentions are related to the dimethylsiloxane series

$$I_{Si} = y + m\frac{\lg V_{N(x)} - \lg V_{N(y)}}{\lg V_{N(y+m)} - \lg V_{N(\ )}}$$

where $V_{N(x)}$ is the retention volume of the substance being analysed, and $V_{N(y)}$ or $V_{N(y+m)}$ the retention volumes of the linear dimethylsiloxanes with y or $(y + m)$ silicon atoms.

An advantage of this system is that the substances belong to the same class, but a slight disadvantage is the difficulty of carrying out a comparison with the retentions obtained on the basis of other standards.

One of the most important correlations between retention and structure is the relationship between the retention and the number of groups or atoms of the same type (analogous to the relationship between the logarithm of the retention volume and the number of methylene groups in homologous series of organic compounds). These relationships have been used to identify the products of the synthesis of mixed hydrides of silicon and germanium, which were obtained in small quantities and were present as mixtures in the reaction product[44].

Some authors have reported deviations from the linear dependence of the logarithm of the retention volume on the number of carbon atoms in series of organometallic compounds[45,46], and this must be taken into account in correlation calculations. The extended additivity scheme for the calculation of the retention volume has not been used. A retention volume calculation scheme, developed for the calculation of thermochemical quantities[47], has proved useful.

The additivity of the logarithm of the retention volume and the retention index has led to the development of a method of calculation for asymmetric compounds from the retention values for symmetric compounds[48-50]. The retention volumes for compounds of the type $R_2MR'_2$ were calculated from those of symmetric organometallic compounds of the type R_4M formed by silicon, germanium[48,49], and tin[50].

Retention volumes for compounds in which the two parameters change simultaneously (for example cyclosiloxanes containing two different siloxane groups in the ring) can be represented by means of nomograms[51] (Fig. 2).

IV. GAS CHROMATOGRAPHY OF ORGANOMETALLIC COMPOUNDS OF GROUPS II AND III

The gas-chromatographic analysis of organometallic compounds of the first group by the direct method is apparently impossible, because of the low volatility of these compounds. The reaction chromatography of organometallic compounds of the first group is examined in section VI.

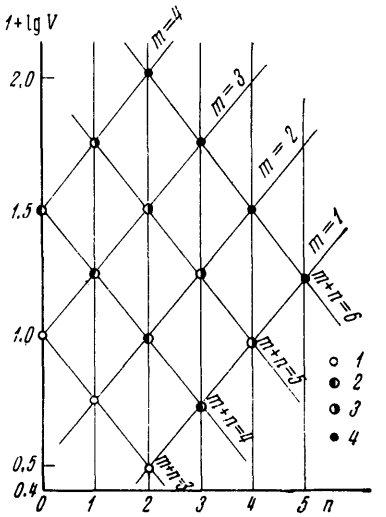


Figure 2. Dependence of the logarithm of the retention volumes of methylpropyldimethylcyclosiloxanes on n, where $n = 0-5$, $m = 0-5$, and $m + n = 3-6$. *1*) Cyclotrisiloxanes, *2*) cyclotetrasiloxanes, *3*) cyclopentasiloxanes; *4*) cyclohexasiloxanes.

Table 1.

Type of compound	Conditions of analysis	Detector	Notes	References
Et_nM, M—Be, B, Zn, Al, Sn, Pb	Glass column. 1 m x 4 mm, sorbent: Chromosorb W + paraffin and diphenylamine (85 : 15), 73°, 143°	Catharometer		38
RHgX	Steel column. 0.19 m x 3 mm, sorbent shimalite + 25% diethylene glycol succinate, butane-1,4-diol succinate, silicone DC-550, 170–200°	Flame-ionisation		23, 27, 60, 63,
RHgX	Steel column. 2 m x 3 mm, glass column, 2.75 m x 4 mm, carrier Chromosorb W + 5% polyethylene glycol succinate, flusine + 1.5% polyethylene glycol, 140–150°	Catharometer, electron-capture		25, 26, 64, 65
RHgX, X=Cl, Br, $OOCCH_3$, SO_4, OH	Column 1–3 m x 3 mm, sorbent Chromosorb W + 10% 13 stationary phases, 120–200°	Electron-capture	Decomposition of RHgX on tricresyl phosphate and butanediol succinate	9

Group II

The chief conditions for the analysis of the ethyl derivatives of beryllium, zinc, boron, and aluminium, and other organometallic compounds of groups II–IV are systematised in Tables 1–3, the data in which give a fairly clear picture of the characteristic features of the gas-chromatographic analysis of this group of compounds.

Organomagnesium and organocalcium compounds have been analysed by reaction chromatography (see section VI).

Organomercury compounds. The high toxicity of organomercury compounds makes it necessary to develop effective methods for the analysis of the biosphere for contamination by these compounds.

Table 2.

Type of compound	Conditions of analysis: stationary phase, temperature	Detector	References
Alkylsilanes	Polyphenylsilicone oil, polyethylene glycol M 1500, 100–175°; silicones SE-30, QF-1, XF-1112	Catharometer	50, 77, 98–100
Chlorosilanes, methylchlorosilanes	Nitrobenzene, 25°; mixture of diethyl phthalate and silicone oil, 104°; benzophenone, 52°; transformer oil, 106°; liquid paraffin and insulating oil, 50–60°; PFMS-4, DS-703, 40°; phthalates, phosphates, silicones	Catharometer, flame-ionisation	101–112
Ethylchlorosilanes	Silicone MS-0150, 90°. PFMS-4, FS-16, 50–100°	Ditto	113–116
Phenylchlorosilanes	Apiezon L + bentone-34 (1 : 1); E-302 120°; silicone MFSD-3, PFMS-4; silicone rubber; Lucopren G-1000, temperature programming; SKTFT-50, 120°; SE-30, temperature programming	»	12, 91, 92, 117–121
Alkylchlorosilanes	Dinonyl phthalate, 40°; nitrobenzene, 40°; PFMS-4, FS-16, 151°; fluorosilicone 169, 160°	»	122–126
Linear and cyclic siloxanes	Silicone DS-703, 125°; Lucopren M, 150–195°; copolymer of diphenylsiloxane and dimethylsiloxane, temperature programming; Apiezon L; PFMS-100, temperature programming; SKTFT-50°; PDMS 80 M, 160–190°; silicone OE-4011, 60°; SKTFT-50, 190–250°; dimethylsiloxane with carboranylene or diphenyl oxide groups, 235–260°	»	40, 127–146
Alkoxysilanes	Silicone G-7100, 175–180°; E-301, 150–180°; SKTFT-50, 175°, 235°		147–150

Methods have been developed for determining organomercury compounds in food[52–56], water and aqueous solutions[26–29], and soil[28,57], based on the extraction of the organomercury compounds from the natural materials, followed by gas-chromatographic analysis.

The selectivity of 16 stationary phases for the separation of alkyl and aryl compounds of mercury has been studied, and it has been established that the best separation is achieved on diethylene glycol succinate and butane-1,4-diol succinate at 160°.[25]

Methods have been developed for the analysis of methylmercury and phenylmercury compounds in various mixtures[28,58–62] (in phenylmercury acetate[28] and in specimens containing sulphides[58]).

For the identification of a number of organomercury compounds, Kitamura and coworkers[62] used a combination of thin-layer and gas chromatography. The conditions for the analysis of compounds of the type RHgX are given in Table 1.

Determination of the retention times of compounds of the type RHgX, with different substituents, on the stationary phases diethylene glycol succinate and butane-1,4-diol succinate established that the retention time is independent of the nature of the substituent X, and is determined by the length of the alkyl radical[24,25]. The fact that the measured retention times of different compounds of the type RHgX are identical is due to the decomposition of these compounds in the volatiliser with the formation of dimethylmercury[66]. The decomposition products were determined by means of flame-ionisation and electron-capture detectors (Fig. 3).

Highly-sensitive selective electron-capture and emission detectors[67] have been used for the determination of micro-quantities of organomercury compounds. A method has been developed for the determination of nanogram quantities of a dialkylmercury by means of a flame-ionisation detector and an MAS-50 detector; this has been proposed for the determination of organomercury compounds in river water[29].

Table 3.

Type of compound	Conditions of analysis	Detector	References
Alkylstannanes, alkyldistannanes, tin hydrides	Column 2 m × 6 mm, sorbent Chromosorb W + 20% polyethylene glycol 20 M, silicone E-301, 200	Catharometer	50
Alkyl- and arylhalogenostannanes	Column 1 m × 4 mm, sorbent celite 545 + 5% silicone oil MS-200, 180°, 200°	Flame-ionisation	185
Mono-, di-, and trihalogenostannanes	Column 2 m × 4 mm, sorbent Sterchamol + 15% silicone OE-4011, 160–180°	Catharometer	186
	Column 2 m × 3 mm, sorbent Sterchamol + 5% polyethylene glycol 20 M, silicone OE-4011, 160–170°	»	35, 187
Dibromodialkylstannanes	Capillary column 2.5 m × 0.3 mm, coated with polyethylene glycol 20 M, 200°	Flame-ionisation	188

The minimal measurable quantity of methylmercury chlorides for the optimal conditions on a column containing butane-1,4-diol succinate is 10^{-12} g when an electron-capture detector is used[24]. A method for the analysis of compounds of the type RHgX is given in section VI.

The chromatographic and biological aspects of the behaviour of organomercury compounds[2], and the analysis of organomercury compounds by photometric, spectroscopic, and chromatographic (paper, thin-layer, and gas chromatography) methods[1] have been reviewed.

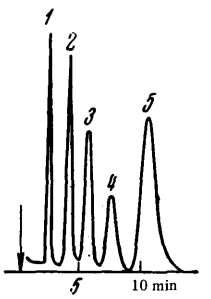


Figure 3. Chromatogram of alkylmercury chlorides. 25% diethylene glycol succinate (4 m × 4 mm), 160°, nitrogen flow rate 80 ml min^{-1}. *1*) Methylmercury chloride; *2*) ethylmercury chloride; *3*) n-butylmercury chloride; *4*) n-pentylmercury chloride; *5*) methylethylmercury chloride.

Group III

The gas chromatography of boron compounds has been carried out chiefly in the analysis of inorganic compounds, for example boron hydrides, borazoles, boranates, and derivatives of boric acid[68–77].

Organoaluminium and organogallium compounds have been analysed by gas chromatography as the ethyl derivatives[37,38]. It should be noted, however, that organoaluminium compounds are usually analysed by reaction chromatography (see section VI).

V. GAS CHROMATOGRAPHY OF ORGANOMETALLIC COMPOUNDS OF GROUP IV

1. Organosilicon Compounds

Study of reaction mechanisms and the composition of reaction products. The redistribution of radicals in a number of organometallic compounds often produces a wide range of components with similar structures, the study of which would be difficult by any method other than gas chromatography. Pollard[11,78] and Phillips[48] made extensive studies of the redistribution of tetra-alkyl derivatives of the group IV elements, including silicon (Fig. 4). These studies were subsequently continued[79,80].

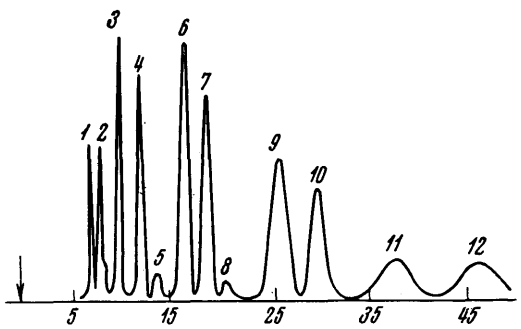


Figure 4. Chromatogram of the products of radical redistribution between $(n\text{-}C_3H_7)_4Si$ and Et_4Ge: *1*) Et_4Si, *2*) $Et_4Ge + Et_3GeCl$, *3*) $Et_3Si(n\text{-}Pr)$, *4*) $Et_3Ge(n\text{-}Pr)$, *5*) $Et_2(n\text{-}Pr)SiCl$, *6*) $Et_2Si(n\text{-}Pr)_2$, *7*) $Et_2Ge(n\text{-}Pr)$, *8*) $Et(n\text{-}Pr)_2GeCl$, *9*) $EtSi(n\text{-}Pr)_3$, *10*) $EtGe(n\text{-}Pr)_3$, *11*) $(n\text{-}Pr)_4Si$, *12*) $(n\text{-}Pr)_4Ge$.

The redistribution of alkoxy-groups or methyl groups with alkoxy-groups between silicon and phosphorus atoms or silicon and tin atoms takes place with difficulty[79]. Gas chromatography has been used in this case for the analysis of small quantities of products of the redistribution of the radicals, which would be extremely difficult to study by other methods. The analysis was carried out with 25% silicone oil on celite at 100–150°.

Redistribution in sterically hindered tetra-alkylsilanes containing isopropyl and isobutyl groups has been studied[80]. The deviation of the distribution of the reaction products from the statistical distribution is particularly marked for radicals with a long hydrocarbon chain. The specific retention volumes of the redistribution products were measured on E-301 methylsilicone (15% on Sil-o-cel) at 150–200°. A remarkable feature is the nonlinearity of the graphs giving the dependence of the logarithm of the retention on the number of carbon atoms (or number of radicals of the same type) for isopropylsilane, n-pentylsilane, and isobutylsilanes; this is apparently due to the steric influence of the atoms in the molecules of the substances being separated. Deviation from linearity has been observed in other analogous cases[81]. The exchange of alkyl radicals between heterocyclic organosilicon compounds has been studied[82,83]; in the first of the works cited, the reaction between hexamethylcyclotrisilathiane and nonamethylcyclotrisilazane was investigated, and two new cyclosilathiazanes were studied. The redistribution of methyl and ethyl radicals in alkylcyclotrisilazanes has been studied[84]. The reaction products were separated by gas chromatography with a detector sensitive towards nitrogen. The compounds were identified more accurately by NMR.

The products of various other reactions have been studied by gas chromatography[85-93]; the composition of the products of the reaction of methyl chloride with a copper–silicon alloy has been determined[86]; and the products of the reaction of hexamethyldisilazane and polymethylchlorosilane have been studied[87].

It has been proved by gas-liquid chromatography that in the presence of iron pentacarbonyl, ethers are split by triethylsilane with the formation of triethylalkoxysilane and hydrocarbon. The alkoxysilanes were analysed on a column containing 5% silicone elastomer on Chromosorb R at 134°.[88] The composition of acyl compounds of silicon has been studied by gas-chromatographic analysis of the reaction products[89].

The products of the catalysed formation of 1,1-dimethylcyclopentasilane were studied by Nametkin and coworkers[90] by gas chromatography. The electrophilic chlorination of phenylchlorosilanes and benzylchlorosilanes has been studied[91,92]. It has been established that the ratio of the quantities of meta- and para-isomers obtained depends on the type of catalyst.

Gas chromatography has been used to study the equilibrium constants of reactions of methylphenoxysilanes and phenylchlorosilanes[93]. Polymethylsiloxane was used as stationary phase, at 230°.

The products of the pyrolysis of phenyldimethylsilane[94,95], aryltrimethylsilanes[19], and tetramethylsilanes[96] have been studied, and the products of the thermal decomposition of tetra-ethoxysilanes have been analysed[97]. The conditions for the analysis of organosilicon compounds of various types are given in Table 2.

Organosilicon compounds containing hetero-atoms in the molecule. Bortnikov[5-7] used gas-liquid and gas-adsorption chromatography to separate organometallic compounds of group IV containing a bond between two silicon, germanium, or tin heteroatoms, and to separate heterocyclic compounds containing silicon and germanium atoms. Various thermodynamic parameters of *cis*- and *trans*-isomers of 1,2-bis(trimethylsilyl)-substituted ethylenes and their germanium analogues have been determined on graphitised carbon black and Apiezon L[5].

The processes of intermolecular sorbate–sorbent interaction in solution and on the surface of an adsorbent have been studied for organometallic compounds of the type $Et_3M\text{–}M'Et_3$ (M and M′ = Si, Ge, and Sn). The separation of these compounds on columns containing Apiezon L, 20 M polyethylene glycol, and graphitised carbon black has been studied. The absolute retention volumes and differential heats of adsorption and dissolution were measured, and the electronic polarisabilities of the compounds were determined[6].

It has been found that graphitised carbon black is a

promising sorbent for the separation of various organometallic compounds, containing two or three hetero-atoms, and sterically hindered silicon-containing ortho- and para-isomers of phenol derivatives[7].

The analysis of impurities is necessary in the study of the purity of monomeric materials in the production of highly pure substances for semiconductor technology (silicon dioxide, silicon carbide) and in the production of polymers.

A number of authors[151-155] have determined impurities in monomeric organosilicon compounds. Traces of dimethyl ether, ethanol, and benzene have been determined in triethoxysilane, trichlorosilane, and methyl chloride[152].

Impurities in methyltrichlorosilane—the starting material for the production of single crystals of silicon—have been identified as chlorides and oxide chlorides of boron and phosphorus on a column containing fluorosilicone oil 169 and DS-701 silicone oil[153]. Impurities in the form of derivatives of aluminium, iron, magnesium, and calcium were absorbed by the stationary phase, and the concentration of metals was reduced below 10^{-6}–10^{-7} wt.%.

Impurities in trichlorosilane were determined on a glass column containing silica gel modified with trimethylchlorosilane[33]. The carrier gas was dried thoroughly, and the concentration of moisture was 5×10^{-4} mole %. Methanol, ethanol, propane, 2-methylpropane, butane, ethyl chloride, silicon tetrachloride, and methylchlorosilane were identified by comparing the signals from thermo-ionic and flame-ionisation detectors. The sensitivity of the determination was 1×10^{-4} – 5×10^{-2} mole %.

The vat residues remaining after the fractional distillation of commercial dimethyldichlorosilane were found to contain traces of ethylchlorosilane, tetramethyldichlorosilane, and hexamethyldichlorotrisiloxane. The individual components were separated by preparative chromatography[154]. Traces of cross-linking agents in the raw material for the production of silicone rubbers have been determined[136]. Traces of bis(dialkylsilyl)arenes, arylsilanes, and halogenobenzenes in the products of the manufacture of monomers for silicone rubbers were identified on a column containing 5% of an arylene siloxane polymer with the formula $[-SiMe_2-Ar-SiMe_2-O-]_n$, where Ar = $-C_6H_4-$ and $-C_6H_4-O-C_6H_4-$, at 141–146°.[155] Traces of water have been determined in polyorganosiloxanes and the carrier gas in the analysis of readily hydrolysed organosilicon compounds[39,156].

Preparative chromatography of organosilicon compounds. Preparative chromatography has been used to separate the components of complex reaction mixtures[153,154,157,158]. The method has also been used to separate a number of deuteriated organosilicon compounds. Deuteriated methylethoxysilanes were separated on a column (7 m × 33 mm) containing 20% dinonyl phthalate on Inzenskii brick at 95°. 1,4-Bisdeuteriomethyltetrasiloxane was isolated on a column (4.8 m × 17 mm) containing 20% SKTFT-50 on S-22 celite at 154°.[157]

Chromatographically pure chlorosiloxanes have been isolated on a column (4.8 m × 17 mm) containing as sorbent 20% SKTFT-50 on S-22 celite at 150–190° in order to convert them into methylated and deuteriated derivatives for mass-spectrometric studies[158]. The purity of the products was 99.2%.

Isomeric high-boiling organosilicon compounds have been isolated by micro-preparative chromatography[159]. The use of a highly efficient trap packed with filter material increased the efficiency of recovery to 95%.

Turkel'taub[160,161] examined the possibility of the preparative isolation of high-boiling organosilicon compounds (b.p. 500–600°C) and proposed organosilicon stationary phases for preparative chromatography[162].

Determination of the physicochemical properties of organosilicon compounds. Gas-liquid chromatography can be used to solve such problems as the choice of separating agent for the extractive separation of mixtures of methylchlorosilanes[163], the determination of the solubility of nitrogen and oxygen in organosilicon liquids[164], and the study of the molecular weight distribution of polydimethylsiloxanes[132].

Gas chromatography has been used most widely for the determination of the saturated vapour pressures and boiling points of organosilicon compounds on the basis of their retention values on non-polar stationary phases[11,42].

2. Organogermanium Compounds

There are relatively few papers on the gas chromatography of organogermanium compounds[5,11,41,44,49,165-172]. Gas chromatography has been used for the first time for the analysis of silicon and germanium hydrides[44,165-167], for the separation of tetramethyl derivatives of germanium on a column containing Apiezon L at 60°,[99] and in the determination of the percentage composition of azeotropic mixtures of trimethylgermanium chloride and diethyl ether on a stationary phase of DS-550 methylsilicone at 70°.[168]

Gas chromatography has been used to study the redistribution of the radicals of tetra-alkyl derivatives of germanium[11], to determine the products of the alkylation of alkylchlorogermanes[170] and the electrophilic chlorination of alkylchlorogermanes[171], and to identify organogermanium compounds in the products of the exchange reaction of bis(triethyl)germylmercury with organotin halides[172].

The additivity method for the calculation of the retention times of unsymmetrical compounds from data on the retention of their symmetrical analogues has been applied for the first time for organogermanium and organosilicon compounds[48,49]. Organogermanium compounds were separated on a column containing squalane (2–13%) or a column containing a mixed phase consisting of 3% squalane and 3% phenylsilicone 702 at 100–150°.

Retention data have been published for a number of organogermanium compounds[41,48,49,125].

Gas-adsorption and gas-liquid chromatography have been used to separate the *cis*- and *trans*-isomers of 1,2-bis(trimethylgermyl)-substituted ethylenes and their silicon analogues[5] on graphitised carbon black and Apiezon L. The retention volumes and the heats of adsorption and dissolution have been measured for these compounds.

3. Organotin Compounds

The first papers on the gas-chromatographic analysis of organotin compounds appeared in 1960–1961[13,99,173-175].

Tetramethyl-derivatives of tin, germanium, silicon, and lead were analysed by Pollard[99] on a column containing Apiezon L at 60°. The preparation and chromatographic analysis of perfluorovinyltin derivatives have been described[173,174]. Matsuda[175] used gas chromatography for the analysis of tin derivatives of the type R_nSnX_{4-n}, where R represents radicals from methyl to pentyl, and X = chlorine, bromine, or iodine. The stationary phase was DS-550 silicone, the temperature 170°, and the column length 3 m.

Study of reaction mechanisms and the composition of reaction products. Gas chromatography has been used to identify the products of the reaction of tetra-alkyl compounds of tin with tin tetrachloride and tetrabromide[176] and the redistribution of the radicals of tetra-alkyl derivatives of group IV metals[11] (Fig. 5).

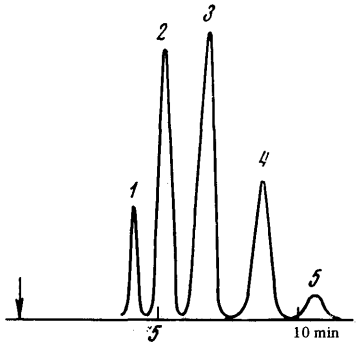


Figure 5. Chromatogram of the products of radical redistribution between $(n\text{-Pr})_4Sn$ and $(n\text{-Bu})_4Sn$: *1*) $(n\text{-Pr})_4Sn$, *2*) $(n\text{-Pr})_3Sn(n\text{-Bu})$, *3*) $(n\text{-Pr})_2Sn(n\text{-Bu})_2$, *4*) $n\text{-PrSn}(n\text{-Bu})_3$, *5*) $(n\text{-Bu})_4Sn$.

The products of the redistribution of the radicals were identified on the basis of the linear dependence of the logarithms of the retention volumes on the number of carbon atoms or the number of substituents of the same type.

Advantages of gas chromatography as a method for studying the redistribution of the radicals include not only the simple and reliable identification and effective separation of the reaction products but also the possibility of carrying out the reaction with extremely small quantities of material (0.002–0.01 mole).[11] The separation of the reaction products was carried out on a 2 m column containing 15% squalane E-301 on S-22 Sil-o-cel. The temperature of the analysis varied in the range 100–250°, depending on the composition of the reaction products.

The use of gas chromatography made it possible to study the exchange of methyl and alkoxy groups between tin and silicon atoms or between tin and phosphorus atoms[77], the hydrostannation of unsaturated compounds, and the reactions of trimethylstannane[75,177].

Gas chromatography has been used to identify the products of many reactions: the redistribution of radicals between alkyltin trichlorides and compounds of the type $RSnR'_3$,[178] the radiolysis of methyl and ethyl derivatives of tin[179], the reactions of tetra-alkyl derivatives of tin and germanium under the influence of ^{60}Co γ-radiation[32], the thermal degradation of tetrabutyltin[180], the reactions of tetra-alkyl-derivatives of tin with boron trichloride[181] and of metallic tin with alkyl halides[182], the reactions of bis(trifluoromethyl)diazomethane with organotin compounds[183], and the photolysis of tetramethylstannane[184].

The analysis of organotin compounds of different types is represented in Table 3.

Retention values have been published for various organotin compounds[11,41,45,50,189].

Putnam[45] measured the retention indices of 14 organotin compounds of the type R_4Sn on three stationary phases[45]. The retention indices of the organotin compounds are slightly larger for polar stationary phases, particularly in the case of unsaturated radicals. The ratio of the retention index to the molecular weight for a polar column shows a correlation with the refractive index of the organotin compound. The dependence of the retention indices on the number of carbon atoms, the molar refraction, and the boiling points has been given, and can be used for the approximate estimation of these quantities for organotin compounds.

With temperature programming, the indices of organotin compounds on a non-polar phase depend little on the rate of heating and change in the same sense as the molar refractions of these compounds[189].

Some deviations from the linear dependence of the logarithm of the retention volume on the number of carbon atoms in homologous series of organotin compounds have been noted[11,45,46]; these must be taken into account in the calculation of retention values by the additivity scheme. These deviations are apparently due to the mutual screening of the tin atom and the methyl groups from the interaction with the molecules of the stationary phase[46].

Preparative chromatography has not yet found extensive application for the separation of organotin compounds. Only the preparative purification of tetramethyltin and tetraethyltin on a column (13 m × 25 mm) containing 18% polyethylene glycol 400 has been described. A 10 ml specimen was purified in 40 min. The concentration of impurities in the product was 10^{-3}%.[190,191]

The determination of impurities in tetrabutyltin and the analysis of alkyltin halides by reaction chromatography are examined in section VI.

Some additional information on spectroscopic and chromatographic methods in the analytical chemistry of organotin compounds is given in two reviews[3,4].

4. Organolead Compounds

Organolead compounds are widely used as additives in motor fuel. Before the development and comprehensive application of chromatographic methods, the analysis of alkyl compounds of lead in petrol involved the determination of the total lead content. In the earliest work[99,192,193] on the gas-chromatographic analysis of organolead compounds, the components separated on the chromatographic column were detected by means of a spectrophotometer or catharometer.

Lovelock and Zlatkis[194] were the first to use for this purpose an electron-capture detector, the sensitivity of which towards organic compounds of lead is several times greater than its sensitivity towards hydrocarbons. The use of an electron-capture detector helped to solve the problems of the identification of complex mixtures.

In addition to organic compounds of lead, petrol always contains alkyl halides which prevent the successful separation of the mixture. An additional column containing as sorbent 20% polyethylene glycol, saturated with silver nitrate, on Chromosorb W treated with 8% potassium hydroxide, was proposed for the separation of alkyl halides[195]. This column was placed after a separating column containing 15% methylsilicone SE-30 on Chromosorb W. 1,2,3-Tris(2-cyanoethoxy)propane[196] and Apiezon L[197] have also been used for the separation of alkyl compounds of lead.

Soulages[10,198] developed a method for the simultaneous

determination of alkyl compounds of lead and alkyl halides in petrol. The analysis involved the separation of the alkyl compounds of lead and the alkyl halides from the hydrocarbons of the petrol on a sorbent consisting of 10% polyethylene glycol 400 on Chromosorb P and hydrogenolysis of the alkyl-lead compounds and alkyl halides at 140° on nickel deposited on Chromosorb P. The reduction products methane and ethane were separated on a column containing active carbon, modified with 3% vaseline at 70°. An electron-capture detector was used.

The above method was used in subsequent work by the same author for the determination of five methylethyl derivatives of lead and alkyl halides in petrol[10]. The separation was carried out on a stationary phase consisting of 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P, treated with 1% potassium hydroxide at 80°.

The identification of mixtures of organolead compounds is made difficult by the lack of pure specimens of the alkyl compounds of lead for the calibration of the detectors. Soulages[22] put forward a simple method of identification with thermal-conductivity and flame-ionisation detectors. The catharometer recorded the alkyl compounds of lead and the alkyl halides separated on the chromatographic column. Simultaneously, the flame-ionisation detector recorded, in the form of methane and ethane, the products after hydrogenolysis. This method was used to identify a mixture of tetramethyl-, tetraethyl-, trimethylethyl-, dimethylethyl-, and methyltriethyl-lead, dichloroethane, dibromoethane, and toluene, separated on a column containing 10% polyethylene glycol 400 and 1% tetrakis(2-hydroxypropyl)ethylenediamine on Chromosorb W.

In the determination of alkyl compounds of lead in aromatic petrols, an additional column containing Apiezon L was used for the separation of the aromatic hydrocarbons. The alkyl compounds of lead were separated on a sorbent consisting of 10% 1,2,3-tris(2-cyanoethoxy)propane on silanised Chromosorb W at 75° or 85°.[199] The chromatogram of the separated products is shown in Fig. 6.

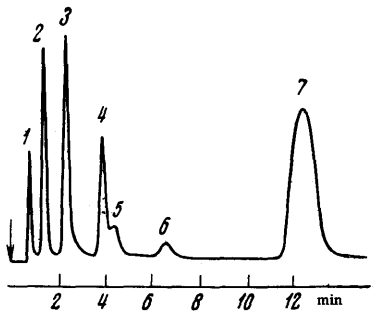


Figure 6. Chromatogram of alkyl compounds of lead, 10% 1,2,3-tris(2-cyanoethoxy)propane (4 m × 3 mm), 85°, nitrogen flow rate 30 ml min^{-1}. *1*) Me_4Pb, *2*) Me_3PbEt, *3*) Me_2PbEt_2, *4*) $MePbEt$, *5*) $C_2H_4Cl_2$, *6*) Et_4Pb, *7*) $C_2H_4Br_2$.

A combination of gas chromatography and atomic-absorption spectroscopy has been used for the quantitative determination of organolead compounds in petrols[200]. The quantitative analysis does not require the calculation of correction coefficients.

All lead compounds are highly toxic, and their concentration in the surrounding atmosphere must be strictly controlled. In the analysis of organolead compounds in air, the problems of concentration of the specimen immediately arise. The use of Yanak's method[201] of concentration, involving the passage of air through an absorbing column filled with the sorbent used in the separating column, has been proposed[31]. Air was forced by means of a pump through a column (8 cm × 1 mm) containing 10% silicone SE-52 on Chromosorb P for 10–15 min. After the concentration, the column was heated rapidly, and the lead compounds were introduced into the chromatographic column, on which the separation was carried out at 80°. An equation was put forward for calculating the concentration of alkyl compounds of lead in air.

VI. REACTION CHROMATOGRAPHY OF ORGANOMETALLIC COMPOUNDS OF GROUPS I–IV

Many organometallic compounds of groups I–IV have a low volatility and are unstable towards atmospheric moisture and oxygen. It is difficult to analyse these compounds by classical methods of gas chromatography, so that in most cases it is not the organometallic compounds themselves, but their transformation products, which are analysed. The version of gas-chromatographic analysis in which chemical reactions are used to convert the substances into forms more convenient for analysis is called reaction chromatography. We shall subsequently use this term in the description of this type of work.

GROUP I

Reaction chromatography has been used for the analysis of organic compounds of lithium, sodium, and potassium, which in most cases are solid, almost non-volatile compounds. These are converted into more volatile compounds by hydrolysis. A system of two chromatographs[202] has been used for the analysis of solutions of vinyl-lithium in tetrahydrofuran. The specimen was hydrolysed on the first chromatograph in an additional column containing hexane-1,2,6-triol on Chromosorb. The ethylene liberated on hydrolysis was identified and determined quantitatively on a column containing 20% dodecyl phthalate on Chromosorb W at 75°. A second chromatograph, connected to the first, was used to determine the trace components present in the ethylene, such as acetylene and buta-1,3-diene, on a sorbent consisting of 20% dimethylsulpholane on brick.

Reaction chromatography has been used to study a number of reactions: the metallation of organic compounds with organopotassium compounds[203–205], the kinetics of the polymerisation of butadiene, isoprene, and styrene in the presence of an alkyl-lithium[206], the reaction of epichlorohydrin with butyl-lithium[207], and the products of the reaction of methylcyclopentane in the presence of benzylsodium[208].

GROUP II

Organomagnesium and organocalcium compounds, like the organic compounds of the group I metals, have a low volatility and are unstable to hydrolysis.

1. Organomagnesium Compounds

The conversion of these compounds into more volatile compounds by hydrolysis or by exchange with alkyltin and alkylsilicon halides has been proposed[209–213].

Reaction chromatography has been used for the first time for the analysis of ethylmagnesium iodide solutions, which were hydrolysed with phosphoric acid in a micro-reaction vessel. The gaseous products were introduced into the chromatographic column through a by-pass line and separated on a column with activated silica gel.

The concentration of solutions of partly decomposed Grignard reagents (*p*-t-butylphenylmagnesium bromide) was determined by double chromatographic analysis[210]. The quantity of aromatic hydrocarbon formed by the decomposition of the Grignard reagent was first determined by direct gas chromatography on a column containing polyethylene glycol. The solution being analysed was then hydrolysed with methanol, and the quantity of t-butylbenzene liberated was determined. The results from the two analyses were used to calculate the true concentration of Grignard reagent in the solution. This method for the analysis of aryl Grignard reagents was subsequently used in a study of the kinetics of the reaction of alk-1-enes with phenylmagnesium bromide[211].

Tributyltin chloride has been used as reagent in the analysis of vinylmagnesium chloride[212]. This reaction gave vinyltributyltin, which was separated from the reaction products on a column containing 20% phenylsilicone DS-550 with temperature programming from 120° to 210° at a rate of 15 deg min^{-1}. This method of analysis appears more promising, since the reaction mixture contains a smaller number of components. The reaction with dimethylphenylchlorosilane has been used for the analysis of methyl Grignard reagents[213]. The trimethylphenylsilane obtained was determined quantitatively by the internal-standard method.

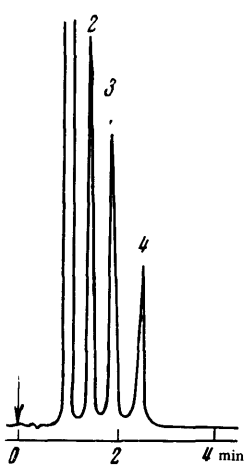


Figure 7. Chromatogram of the products of the hydrolysis of the complex of dioxan with phenylcalcium iodide: *1*) diethyl ether, *2*) benzene, *3*) toluene (standard), *4*) dioxan.

2. Organocalcium Compounds

Reaction chromatography has been used for the analysis of organocalcium compounds isolated for the first time in the individual state in the form of complexes with dioxan and amines[214]. The solution of the complex of dioxan and arylcalcium iodide in ether was decomposed with water. The CaI(OH) precipitate was separated by centrifuging. The aromatic hydrocarbon and dioxan obtained on hydrolysis were separated on a column containing 5% diethylene glycol succinate at 94° (Fig. 7). The quantitative determination of the aromatic hydrocarbon and dioxan was carried out by the internal-standard method. The method of analysis of organocalcium compounds by gas chromatography has made it possible to develop an optimal method for the preparation of diphenylcalcium.

3. Organomercury Compounds

There is only one published paper on the reaction chromatography of organomercury compounds; this describes the identification of a mixture of alkylmercury halides by means of the reactions with various sulphur-containing substances—sodium thiosulphate and metal sulphides—and metal powders[215]. The method involves double chromatography of the mixture being analysed; the separation is first carried out by the direct method, after which the solution being analysed is treated with various sulphur-containing compounds or passed through an additional column containing metal powder, and subjected to a second separation.

GROUP III

Reaction chromatography has been used chiefly for the analysis of organoaluminium compounds.

Organoaluminium Compounds

Organoaluminium compounds decompose readily under the influence of oxygen and water. The temperatures of the start of the thermal decomposition of these compounds are lower than the boiling points at atmospheric pressure.

Reaction chromatography has been used for the analysis of triethylaluminium, which is a catalyst for the preparation of polyethylene[216].

A solution of triethylaluminium in cyclohexane was evaporated in a stream of hydrogen and passed through a tube filled with 30% lauric acid on Sil-o-cel, connected to the chromatograph. The hydrolysis products were determined in two stages; ethane and butane were first determined on a column containing dibutyl phthalate, after which hydrogen and ethane were determined on a column containing silica gel.

In the analysis of triethylaluminium and tripropylaluminium, these compounds were hydrolysed with n-hexanol, diethylene glycol, and its mixture with aqueous sulphuric acid solution[217,218]. Hydrogen, methane, ethane propane, and butane were separated on dimethylsulpholane deposited on silica gel, and dinonyl phthalate on celite at 30°.

Palamarchuk[219] put forward a method for the analysis of triethylaluminium, in which the specimen was decomposed directly in the entry compartment of the reaction vessel. The specimen in an atmosphere of dry nitrogen was decomposed with diethylene glycol, and the hydrolysis products were transferred by the carrier gas into a separating column containing alumina. If the triethylaluminium contained impurities, for example diethylaluminium oxide, the alcohol and ethane liberated in its hydrolysis were separated on a column containing a mixed sorbent of 15% tricresyl phosphate on Polysorb and 10% squalane on Teflon.

Gas chromatography has been used for the analysis of the products of the reaction of α, ω-dienes with di-isobutyl-lithium hydride[220] and in the study of the kinetics of the reaction of alkyl compounds of metals with alkenes[221].

GROUP IV

Reaction chromatography has been used in the analysis of organosilicon and organotin compounds.

1. Organosilicon Compounds

Reaction chromatography has found extensive application in the structural analysis of organosilicon compounds. This method was developed by Franc and coworkers[222-227]. The method involves a number of reactions with BF_3, BCl_3, H_2SO_4, HNO_3, HI, Zn, NaOH, and KOH in a special reaction vessel (Fig. 8) to determine the structure of the organosilicon compounds and to detect functional groups. In the reaction with BF_3, the organosilicon compounds are split at the siloxane bonds, halogen and hydrogen are replaced by fluorine, and the phenyl radical is split off as benzene[225,227]. In hot concentrated sulphuric acid, alkyl-, aryl-, chloroalkyl-, and chloroaryl-silanes are split with the formation of hydrocarbons and alkyl halides[223,226,227]. Hydrogen iodide splits alkoxy-compounds with the formation of alkyl iodides[223,227]. Si–H and Si–Si bonds are split by potassium hydroxide solution with the formation of hydrogen. The reaction products are analysed by gas-liquid chromatography and paper chromatography[227].

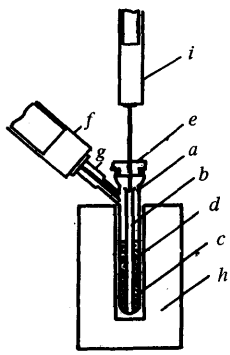


Figure 8. Glass reaction vessel for carrying out decompositions before application to the chromatographic column: *a*) glass vessel, *b*) glass tube, *c*) layer of calcium fluoride, *d*) layer of porous material (Risorb) [sic], *e*) silicone rubber stopper, *f*) 10 ml syringe, *g*) silicone rubber tube, *h*) copper block, *i*) 1 ml syringe.

A method of reaction thermal analysis has been developed, which makes it possible to determine the nature of a functional group and to establish the structure of a molecule on the basis of the reaction between the substance being studied and a suitable reagent, with temperature programming[225,226]. The method has been used to determine the structure of linear and cyclic polyorganosiloxanes by splitting these compounds with sulphuric acid. The relationship between the structure of the substance being studied and the temperature at which the separation of individual functional groups took place was examined. The thermograms of polyorganosiloxanes were given. A number of authors[228-230] have also used reaction chromatography for the analysis of organosilicon compounds. For the determination of Me_3Si-, $Me_2Si=$, and $MeSi\equiv$ groups in methylpolysiloxanes, it has been suggested that the polymer be depolymerised by the action of $2BF_3 .(C_2H_5)_2O$, with subsequent chromatographic analysis of the methylfluorosilanes produced[228]. The separation and quantitative analysis of a mixture of phenylmethyldichlorosilane, phenyltrichlorosilane, and silicon tetrachloride were carried out by converting them into the corresponding fluoro-derivatives on a column containing Na_2SiF_6.[229]

Gas chromatography has been used to study thermal processes taking place in polymers[231]. Pulse pyrolysis under chromatographic conditions has been used for the determination of vinyl groups in alkylcyclosiloxanes[232].

2. Organotin Compounds

Reaction chromatography has been used for the analysis of a mixture of alkyltin halides, which are thermally unstable and readily undergo radical redistribution[233,234].

Butyltin, octyltin, and phenyltin halides react with Grignard reagents with the formation of the more stable tetra-alkyl compounds, which have lower boiling points. For example, butyltin bromides are converted quantitatively into the butylmethyl analogues by the action of methylmagnesium bromide. The separation and quantitative determination of organotin compounds has been carried out on a column containing 20% methylsilicone SE-30 with temperature programming, from 50° to 270°.

Pyrolytic gas chromatography has been used for the determination of impurities in tetrabutyltin[235]. The substances separated on the chromatographic column were subjected to thermal decomposition, and the pyrolysis products in turn were separated on a column containing methylsilicone E-301 and recorded by means of a flame-ionisation detector. A number of impurities with general formula $(R_1)_nSn(R_2)_{4-n}$ (where R_1 and R_2 represent ethyl, methyl, butyl, or s-butyl) were identified.

VII. FUTURE DEVELOPMENTS IN THE GAS-CHROMATOGRAPHIC ANALYSIS OF ORGANOMETALLIC COMPOUNDS

The introduction of gas chromatography in the chemistry of organometallic compounds took place in the period 1960–1965. The gas chromatography of organometallic compounds can now be regarded as a sufficiently well-developed field of application of the method, but its possibilities have not yet been exhausted. We can expect an extension of the range of classes of organometallic compound analysed by gas chromatography, and also of the range of problems to be solved and versions of the chromatographic methods used.

Up to the present, almost no use has been made of capillary gas chromatography in the analysis of organometallic compounds; this is due to the adsorption of the organometallic compounds to be separated on the walls of the capillary, and the difficulty of detecting micro-quantities of organometallic compounds. When these difficulties have been eliminated, the use of capillary chromatography

for the separation of a large number of mixed isomeric compounds of several elements will appear particularly promising.

By analogy with the gas chromatography of organic compounds, we can expect the development of methods of combined chromatographic analysis (combination of gas and thin-layer, gas and liquid, and gas and paper chromatography).

Up to the present, only a few papers have been published on the use of highly sensitive selective detectors for organometallic compounds. An extension of the range of types of highly sensitive detector, and their more intensive use in the analysis of micro-components and the identification of organometallic compounds, appear probable.

The use of chromatography–mass spectrometry (for organomercury [63,236] and organosilicon [237] compounds) will apparently be extended after the elimination of a number of difficulties encountered at present, namely the non-availability of the mass spectra of many organometallic compounds, the complexity of the analysis of organometallic compounds under chromatography–mass spectrometric conditions, and the phenomena of instrument memory.

Gas chromatography is extensively used for the determination of the physicochemical characteristics of substances, the study of reaction mechanisms, and the study of catalytic processes [238].

We can expect the development of methods associated with the determination of physicochemical characteristics, and an extension of the types of reaction carried out under chromatographic conditions (catalytic reactions involving organometallic compounds).

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