

CHREV. 124

GAS CHROMATOGRAPHIC ANALYSIS OF ORGANOSILICON COMPOUNDS

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1. INTRODUCTION

The high thermal stability of organosilicon compounds (OSC) is one of the main factors accounting for their wide application in gas-liquid chromatography (GLC). Their main uses are as stationary phases and as reagents for derivatization in the gas chromatography of various organic compounds. For instance, a Handbook of Gas Chromatography¹ lists 70 organosilicon stationary phases (SP) employed in half of the total number of GLC separation procedures. Another important property of OSC is their capacity to reduce the polarity of chromatographic supports by reaction with the surface hydroxyl groups. Similar procedures may be employed to increase the thermal stability and volatility of a number of polar organic compounds, such as carboxylic acids, steroids, carbohydrates and amino acids. Over 1000 publications have been reviewed²⁻⁶ that deal with the problem of the silylation of organic compounds and the analysis of trimethylsilyl (TMS) derivatives.

On the other hand, organosilicon compounds lend themselves readily to separation by GLC. However, only about 250 publications (less than 1% of the total number of publications on GLC) are connected to varying degrees with the gas chromatography of OSC. Several reviews^{3,7-10} have surveyed the problems of sampling, the choice of stationary and mobile phases for the separation of some typical mixtures (mostly monomers) and the detection and pyrolysis of OSC.

However, there is no complete survey available of the methods used for OSC separation. The applicability of GLC in combination with other techniques and the gas chromatographic properties of OSC have also been omitted from most

reviews. To fill this gap, we have attempted to review the experimental data bearing on these problems that had been published up to the middle of 1978.

2. RELATIONSHIPS BETWEEN RETENTION PARAMETERS OF ORGANOSILICON COMPOUNDS AND THEIR PHYSICO-CHEMICAL PROPERTIES AND STRUCTURE

The relationships between the structure and properties of substances is a matter of lasting interest in chromatography. Most studies on gas chromatography, at least to some extent, pertain to the problem of the chromatographic behaviour of organic compounds. The chromatography of OSC is not so well documented, the data being scattered in the literature.

The retention of a solute in gas chromatography can be described by using various parameters, such as retention time, retention volume and relative retention values. Retention indices are also frequently used¹¹⁻¹⁵. These methods are inter-related¹⁶, because the physical entity determining the chromatographic properties of substances is invariable, regardless of the type of retention parameter applied.

Several retention parameters analogous to Kováts retention indices have been proposed in the study of OSC. Preisler¹⁷ proposed the use of the homologous series of dimethylcyclopolysiloxanes as a reference series:

$$i = 100n + 100 \left(\frac{\log V_{Ri} - \log V_{Rn}}{\log V_{R_{n+1}} - \log V_{Rn}} \right) \quad (1)$$

where i applies to the substance being studied, and n and $n+1$ to cyclic polydimethylsiloxanes containing n and $n+1$ silicon atoms, respectively.

Garzo and Alexander¹⁸ introduced the so-called dimethylsiloxane number:

$$DN_x = 100 \left(\frac{\log t'_x - \log t'_{D_m}}{\log t'_{D_{m+1}} - \log t'_{D_m}} + m \right) \quad (2)$$

where x is the substance being studied and D_m and D_{m+1} refer to polydimethylsiloxanes with m and $m+1$ silicon atoms, respectively. The use of linear polydimethylsiloxanes as a reference series was reported by Wurst and Churaček¹⁹:

$$I_{St} = y + m \left(\frac{\log V_{N(x)} - \log V_{N(y)}}{\log V_{N(y+m)} - \log V_{N(y)}} \right) \quad (3)$$

where x corresponds to the substance being studied and y and $y+m$ to linear polydimethylsiloxanes containing y and $y+m$ silicon atoms, respectively.

Logarithms of retention volumes and retention indices for homologous series of organic substances are known to be correlated with the boiling temperatures of the solutes:

$$R = a_0 + a_1 T_b \quad (4)$$

where R is the retention index or the logarithm of the absolute or relative retention volume and T_b is the boiling temperature.

There is a fairly good correlation between these parameters, not only for homologues, but also for a much wider range of substances with similar structures. The same relationship is observed in the series of OSC. Bortnikov²⁰ demonstrated that eqn. 4 is valid for a number of organic derivatives containing silicon and germanium. The equations obtained enable to determine the boiling point with 3% accuracy on the basis of gas chromatographic data. Palamarchuk *et al.*²¹ investigated the relationship between the relative retention volumes and the boiling points of the compounds formed during the synthesis of ethylchlorosilane. The resulting diagrams were further used to determine the boiling points of unknown compounds. The departures from literature data never exceeded 4°C. Kirichenko and co-workers²²⁻²⁴, on the basis of temperature dependence data, found the heats of solution of dimethylcyclosiloxanes, alkoxychlorosilanes and ethoxyfluorosilanes and showed them to be correlated with the boiling temperatures. Nickless and co-workers¹⁵⁻³⁰ reported on the redistribution reactions of organo-element compounds.

The same linear correlation was found between the logarithms of retention volumes and boiling temperatures for silicon- and tin-containing derivatives. However, with aromatic derivatives, even for the OSC, the experimental points fail to fit the same line³¹. Rumyantseva and co-workers³²⁻³⁵ studied alkyl-, aryl-, halogen-, chloro- and alkylsilanes, polysiloxanes and other OSC and demonstrated the possibility of determining, on the basis of the boiling temperatures, the logarithms of retention volumes with approximately 2% error. The boiling points of alkoxy-silanes³⁶ and alkylsilanes³⁷ can be determined with $\pm 4^\circ\text{C}$ accuracy using chromatographic data, as reported by Peetre and co-workers. Garzo *et al.*³⁸ also observed the retention indices of chloro-, alkyl-, aryl- and alkoxy-silanes to be linearly correlated with their boiling temperatures. Ainshtein and Shulyatieva³⁹ found the retention indices of 56 alkyl- and arylchlorosilanes to be correlated with the boiling temperatures, but in this instance considerable departures from linearity were observed. Brown and Mazdiyasi¹⁰ reported that isopropoxides of the group IV elements were eluted from the chromatographic column in order of decreasing volatility.

A linear correlation between logarithms of retention volumes and molar volumes was demonstrated by Wurst and co-workers^{41,42} for OSC:

$$\log V_g = V^M K_1 + K_2 \quad (5P)$$

where K_1 and K_2 are constants characteristic of particular classes of organic and organosilicon compounds. Retention may also be represented by:

$$\log V_g = \frac{V_i^M(\delta_L^2 + 2\delta_i\delta_L)}{2.3 RT} + \text{constant} \quad (6)$$

where V^M and δ_i are molar volume and solute solubility parameters, respectively, and δ_L is the solubility parameter of the stationary phase.

The relationship between molar refraction (MR) and the logarithms of retention parameters was investigated by Wurst and co-workers⁴³⁻⁴⁶, who found that for the compounds under study the equation

$$\log V_g = a_0 + a_1 MR \quad (7)$$

was valid, where a_0 and a_1 are coefficients specific for homologous series. Supporting evidence demonstrating the validity of this equation was provided by Ellrén *et al.*³⁶ for alkoxy-silanes. Kirichenko *et al.*²² also found that the heat of solution in alkoxy-chlorosilanes used as stationary phases was well correlated with molar refraction. Ellrén *et al.*⁴⁷ proposed a "refraction number", which is analogous to retention index:

$$N_{D(A)} = 100p + \left(\frac{n_D^{20}(A) - n_D^{20}(C_p)}{n_D^{20}(C_{p+1}) - n_D^{20}(C_p)} \right) \cdot 100 \quad (8)$$

where n_D is refractive index and C is the number of carbon atoms in an n -alkane. The indices (A), (p), ($p+1$) refer to the test-compound and n -alkanes containing p and $p+1$ carbon atoms, respectively. The N_D values were shown to be correlated with retention indices. The above correlation can be employed for the group identification of alkyl- and alkoxy-silanes.

Wurst^{43,44,46} demonstrated a linear correlation between parachor and the logarithms of retention indices for polysiloxanes and alkylchlorosilanes. The coefficients in the equation

$$\log V_g = a_0 + a_1 P \quad (9)$$

are characteristic of the homologous series.

In cases when specific interactions within a particular group of compounds contribute to retention to the same extent, a linear correlation between retention values and molecular mass is observed. Bortnikov *et al.*⁴⁸ reported on the properties of substances in Et_3MH and Et_4M series; it was established that retention volumes tend to increase when the atomic weight of the element M increases. The adsorption and solution properties of organo-element compounds studied by gas chromatography^{20,49,50} revealed a linear correlation between the chromatographically determined values of the heat of solution and adsorption and molecular mass of the solute. A linear relationship between logarithm of retention volume and molecular mass was demonstrated by Preisler¹⁷ for polydimethylcyclosiloxane, methylhydrocyclopolysiloxane and methylethylhydrocyclopolysiloxane series. A similar correlation was noted for nitrogen-containing OSC⁵¹. Similarly, retention indices determined within series of N -substituted saturated nitrogen-containing heterocycles were shown to have the same type of relationship^{52,53}. Retention indices of methyl(2-furyl)silanes, -germanes, -stannanes and -plumbanes of the formula $\text{Me}_{4-n}\text{MFu}_n$ have also been found to increase in parallel with the atomic weight of the element M ⁵⁴.

Several studies have reported temperature dependences of retention values in OSC. Nagy *et al.*⁵⁵ present evidence of a linear correlation between logarithm of effective retention volume measured for members of the same homologous series on the same column at various temperatures with programming of the carrier gas flow-rate. Similar evidence was presented by Nickless and co-workers²⁵⁻³⁰. Wurst and co-workers^{44,56} investigated the temperature dependence of the retention parameters of vinylmethoxysilanes and polydimethylsiloxanes and proposed the equation

$$\log V_g = A + \frac{B}{T} \quad (10)$$

where A and B are constants.

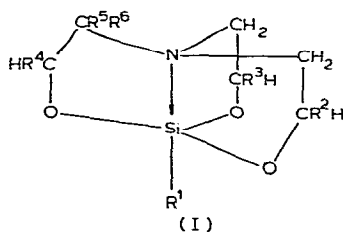
The temperature dependence of retention indices of OSC was studied by Kirichenko and co-workers^{22,57-59}. The retention indices were found to decline with increasing temperature, the temperature coefficient $\partial I/\partial T$ varying with the size of the polydimethylsiloxane ring. Temperature dependence can be used for assigning chromatographic peaks to particular homologous series.

The temperature dependence of retention volumes can also be employed to determine heats of solution in the stationary phase. The dependence of the relative molar heats of solution on the relative molar entropy of solution was studied by Chernoplekova *et al.*⁶⁰. The dependences were found to be identical for silicon, germanium and tin derivatives on non-polar stationary phases, but they varied on polar stationary phases. This finding enables one to discriminate between derivatives of these elements, and to assess the degree of molecular asymmetry and polarity.

Some other physico-chemical properties of solutes have been found to influence retention values. For instance, chromatographic data can be useful in assessing electron polarizability^{20,48-50}. Heat of adsorption has been reported to be linearly correlated with chemical shifts in the NMR spectra of OSC^{20,48-50}.

The dipole moments of solutes are known to be responsible for their capacity for orientational interactions with stationary phase molecules. Ainshtein and Shulyatieva³⁹ presented evidence of correlations between ΔI values and dipole moments for methyl- and phenylchlorosilanes.

The retention indices of a series of C- and Si-substituted silatranes (I) have been measured²⁴⁸. These compounds are characterized by unique ΔI values (as high as



1517 units for phenoxysilatrane on OV-225). The inter-relations between the ΔI values and dipole moments of these compounds can be described by

$$\Delta I = a_0 + a_1\mu \quad (11)$$

This equation permits the evaluation of dipole moments with $\pm 5\%$ accuracy using chromatographic data. The chromatographic properties of silatranes can also be described by using modified Taft equation:

$$\Delta I = a_0 + a_1\sigma^* + a_2E_s^0 \quad (12)$$

Retention is shown to decline with increasing number of substituents on carbon atoms in the α -position with respect to oxygen, the resolution of diastereomers being attainable even on packed columns. The structural element $\equiv N \rightarrow Si \equiv$ provides for 430, 640 and 900 units (Apiezon L, OV-17 and OV-225, respectively). The ex-

tremely high values of the retention indices are probably due to enhanced interaction of oxygen atoms with electron-acceptor groups on the stationary phase as a result of transannular $\equiv\text{N}\rightarrow\text{Si}\equiv$ bond formation.

We also studied the induction effect of the substituent on the appropriate values of 1-(trimethylsilylalkyl)pyrrolidines, -piperidines and -perhydroazepines^{52,53}. It was found that variation in basicity within these series of compounds does not lead to any appreciable changes in the retention values.

The space orientation of fragments in OSC molecules has also been found to affect the retention values. For instance, branched silicon- and germanium-containing organic compounds are characterized by lower retentions than their analogues with normal structures⁶¹. With polydimethylsiloxane pyrolysis products, Garzo *et al.*⁶² demonstrated faster elution for compounds that possessed more compact structures (branched or cyclic) for an equal number of silicon atoms. This observation permitted the preliminary identification of a number of polycyclic siloxanes.

To assess the retention of OSC, one can consider methods of comparative calculations. There have been reports demonstrating that retention indices of alkylchlorosilanes⁶³ and nitrogen-containing OSC⁵¹ can be calculated *a priori* by using the first method of Karapetyantz's comparative calculations⁶⁴.

Several workers⁶⁵⁻⁶⁹ have discussed the correlation between retention parameters measured on different sorbents varying in selectivity. It was found that the homologous series tended to comply with the following equation for non-polar (A) and polar (B) stationary phases:

$$\log V_{u_A} = a_0 + a_1 \log V_{u_B} \quad (13)$$

$$\Delta I = \text{constant}$$

The elution of polydimethylsiloxanes on two stationary phases was studied by Garzo and co-workers⁶⁶⁻⁶⁹. The two phase diagram allows one to discriminate between "isomer lines" and "sub-isomer lines", which can be used to clarify the structure of the components of the mixture. The proposed method for the qualitative analysis of polycyclic organosilicon compounds is also applicable to the gas chromatography of TMS esters of silicic acid⁶⁹. According to Ellrén *et al.*³⁶, retention indices on XE-60 can be estimated using retention indices determined on a non-polar stationary phase (Apiezon L):

$$I^{XE} = kI^{APL} + l \quad (14)$$

Franc *et al.*⁶⁵ studied the chromatographic properties of phenylsiloxanes on polar (A) and non-polar (B) stationary phases. It was demonstrated that in the plots of number of phenyl groups *versus* $\log t_{RB}/\log t_{RA}$, the points corresponding to the same number of phenyl radicals tended to fall closely together, the value $\log t_{RB}/\log t_{RA}$ declining with increasing number of phenyl radicals.

It is known that the introduction of the same structural elements into molecules of different solutes may result in similar increments of the logarithm of retention volumes or retention indices. This accounts for the correlation observed between retention parameters and the number of particular atoms or structural fragments present in the molecule. For instance, the number of silicon atoms in silanes is linear-

ly correlated with the logarithm of specific retention volume⁶¹. The same relationship holds for germanium derivatives. A linear correlation between logarithm of retention volume or retention indices and the number of siloxane units has been reported for polydimethylsiloxanes by Wurst⁴³, Wurst and Dusek⁵⁶ and Rumyantseva *et al.*^{32,33,35}. Kirichenko *et al.*⁵⁹ studied the influence of the ring size on the retention indices of various organocyclosiloxanes and were able to identify compounds containing up to 12 silicon atoms.

Luskina *et al.*⁷⁰ reported that an increase in $\log V_g$ values was linearly related to the increasing size of the ring in the homologous series of oligodimethyl(methyl-dichlorophenyl)cyclosiloxanes. α,ω -Dihydrodimethylsiloxanes were studied by Kochetov *et al.*⁷¹. The increments of I determined for $-\text{O}-\text{SiMe}_2-$ fragments were used to calculate retention parameters for a number of compounds. The accuracy of the calculations was about ± 5 index units. Nomograms for the identification of components in complex mixtures of structurally related compounds were prepared by Yudina and co-workers^{72,73}, based on the finding that methylpropylsiloxane and methyltrifluoropropylsiloxane groups affect retention in a standard manner. Peetre *et al.*³⁷ demonstrated that the retention indices of mixed tetraalkylsilanes and structurally identical tetraalkoxysilanes may be connected by the following equation:

$$I_{\text{alkyl}} = k_1 I_{\text{alkoxy}} + k_2 \quad (15)$$

the correlation coefficient exceeding 0.999. Thus, I values for alkylsilanes can be calculated by using the I values for alkoxy silanes, or *vice versa*, with an accuracy of $\pm 1-2$ units. A linear correlation between the logarithms of the effective retention volumes of two homologous series studied under the same experimental conditions was reported by Nagy *et al.*⁵⁵. The stability of the effects exerted on retention by various structural fragments allowed Berezkin and co-workers⁷⁴⁻⁷⁶ to express the logarithm of the relative retention time of OSC as the sum of contributions by particular bonds or structural elements:

$$\log \tau_i = \sum n_{gj} \Gamma_{gj} \quad (16)$$

where τ_i denotes relative retention time, Γ_{gj} is $\log \tau$ corresponding to the particular set of bonds (structural element) and n_{gj} is the number of such structural elements in the molecule. The increments contributed by the fragment $-\text{CH}_2-\text{CH}_2-$ were shown to be virtually identical for alkanes and alkylsilanes, which makes it possible to predict the chromatographic properties of OSC on the basis of retention data found for the carbon analogues. Similarly, Rumyantseva and co-workers³²⁻³⁵ expressed the retention values of a number of alkyl-, aryl- and halogensilanes, chloroalkylsilanes and polysiloxanes as the sum of individual contributions. Wurst and Churaček¹⁹ measured increments of I_{S_i} values and Garzo and co-workers reported increment values found for retention indices³⁸ and for DN_x ⁶⁶⁻⁶⁸. Kochetov⁷⁷ described retention parameters as the sum of individual contributions. We also demonstrated⁵⁴ that the retention of

compounds of the general formula $\left(\text{C}_4\text{H}_6\text{O} \right)_n \text{M}(\text{CH}_3)_{4-n}$ can be described by

$$I = a_0 + a_1 X_1 + a_2 X_2 \quad (17)$$

where X_1 is the atomic weight of the element M and X_2 is the number of furan rings per molecule. The use of structural increments to determine I values for nitrogen-containing OSC was discussed by Kochetov *et al.*⁵¹. Nagy⁵, Chernoplekova *et al.*⁶⁰ and Ellrén *et al.*³⁶ reported retention values to be linearly correlated with the number of carbon atoms in various groups of OSC. Kirichenko and Markov²² and Preisler¹⁷ demonstrated a linear correlation between retention values and the number of chlorine atoms in solutes.

On the other hand, it is not infrequent to observe a departure from the additivity principle due to the mutual effects of the structural fragments. For instance, such evidence was presented by Ainshtein and Shulyatieva³⁹ for alkyl- and arylchlorosilanes. Semlyen and co-workers^{78,79} demonstrated that the retention values found for chlorosilanes and chlorogermanes on the basis of additive calculations may differ significantly from the experimental data. The differences between the calculated and experimental values were found to depend on the length of the hydrocarbon radicals attached to the silicon atom. Likewise, the retention indices calculated for silatranes fail to comply with the additivity scheme, because the contribution of the structural fragment $\equiv N \rightarrow Si \rightleftharpoons$ is fairly large and it lacks stability.

In many instances, the observed departures from additivity can be taken into account and the appropriate corrections can be made, but this usually results in the creation of too cumbersome models. Kirichenko *et al.*⁸⁰ found increments of retention indices that correspond to particular structural fragments in alkylchlorosilanes and attained a fairly high accuracy in their calculations, as they took account of the effect exerted by the number of carbon atoms in hydrocarbon radicals (m) and the total number of alkyl groups (n):

$$I = \delta I_{SiCl_n} + n(100m)(4-n) \quad (18)$$

It has been established that in methyl- and ethylcyclopolysiloxanes the contributions of MeHSiO and EtHSiO fragments to retention indices are not constant and vary with the size of the ring⁸¹. The relationship between retention indices and the number of members (n) in the ring was described as follows:

$$I = a_0 + a_1\sqrt{n} + a_2n \quad (19)$$

The accuracy of the calculations was ± 5 units. Takacs *et al.*⁸² proposed a method for *a priori* calculations of retention indices for methylchlorosilanes, allowing the assessment of the contributions of atoms and bonds and the interactions with stationary phases^{83,84}.

Pectre and co-workers^{36,37,47,85-88} made a detailed analysis of the chromatographic properties of a large number of tetraalkyl- and tetraalkoxysilanes. A method and an improved computer program adapted for the analysis of complex mixtures when the addition of all necessary n -alkanes is impossible were proposed for the calculations of retention indices⁸⁸. Retention indices of mixed tetraalkoxysilanes were studied³⁶ and it was demonstrated that these compounds are characterized by higher values of I than those calculated using the additivity principle on the basis of their symmetrical analogues. This discrepancy was found to be dependent on the length of

the shortest alkyl chain and on the difference in length between the shortest and the longest chains. The following equation was proposed for the calculation of I :

$$I_{(RO)_4Si} = \Sigma I_{ROSi} + \Sigma(ndk)_{RO-RO} \quad (20)$$

where I_{ROSi} is one quarter of the retention index of $(RO)_4Si$; n is a combination number that is found by multiplying the numbers of the various alkoxy groups attached to the silicon atom; d is the difference in length between the carbon chains of two alkoxy groups; and k is a constant determined by the length of the shortest carbon chain.

The retention indices calculated on the basis of this equation differed from the experimental values, on average, by 1.2 units. The value of the correction term ndk was shown to be determined by the interaction of carbon atoms in various alkoxy groups. The accuracy of the calculations can be further enhanced for alkoxysilanes by using an improved equation⁸⁶ that permits an *a priori* determination of the temperature increment of the retention index. The procedures developed were later extended to tetraalkoxysilanes with branched chains⁸⁷. The increase in the retention indices with the increasing chain length was found to depend on the charge sign of the terminal carbon atom, as revealed by a study with tetraalkylsilanes³⁷. Further, it was assumed that charge alternation takes place in the carbon chain attached to the silicon atom⁸⁹. The introduction of a β -CH₂- group into a tetramethylsilane molecule resulted in an increase of 125.6 units in the I value, whereas with a γ -CH₂- group it was only 67.6 units. Thus, the anomalously low value of I of tetramethylsilane may be due to the negatively charged peripheral part of the molecule hindering its dissolution in the stationary phase. Transition from methoxysilane to ethoxysilane results in a small increase in the I value (by 25 units on OV-17). Apparently in this instance also ethoxysilane shows anomalously low solubility in the stationary phase due to the negatively charged outer surface of the molecule.

The above facts serve to illustrate the existence of various correlation patterns between the structure of OSC and their retention values obtained by GLC. A knowledge of these correlation patterns is of the utmost importance for several reasons. It provides a compact representation of retention data for various classes of substances and helps to predict retention parameters for chromatographically unexplored compounds, to identify components of complex mixtures and to gain an insight into the physico-chemical processes that determine the interactions between solutes and stationary phases. Although *a priori* methods used to calculate retention parameters are not sufficiently accurate to provide unequivocal identification of components in multi-component mixtures, as compared with experimentally obtained data, they are useful in helping to substantiate or disprove hypotheses bearing on the structure of components in test mixtures or, at least, to narrow significantly the scope of the available concepts.

3. DETECTORS FOR GAS CHROMATOGRAPHY OF ORGANOSILICON COMPOUNDS

Thermal conductivity and flame-ionization detectors are the most common detector devices currently used in gas chromatography. The former is conspicuous for its simple construction and reliability in operation. Its applicability to the analysis

of both organic and inorganic compounds offers certain advantages, especially with alkylchlorosilane mixtures, which normally contain trace amounts of inorganic substances that cannot be detected with a flame-ionization detector. An important property of the katharometer is that the separated compounds are not destroyed, which allows fractions to be collected for further investigation, for example, by spectroscopic methods. Frequent cleaning the detector is also avoided. On the other hand, the sensitivity is low and its response is slow, which makes it inapplicable to the analysis of impurities and in capillary chromatography. Like most other detectors, katharometers exhibit a wide variation in sensitivity towards different chemical substances, which cannot be readily predicted on the basis of theoretical assumptions. Response factors found for a katharometer (with helium as the carrier gas) were presented by Hanneman¹⁰ for polydimethylsiloxanes and methyl- and phenylchlorosilanes. The response factors increased (and the sensitivity therefore decreased) with increasing number of units in siloxane polymers and with increasing content of chlorine in chlorosilanes. A similar variation in katharometer sensitivity was noted for methylchlorosilanes by Rotzsche⁹¹. Dearlove *et al.*⁹¹ provided molar and weight response factors to be used for alkoxysilane series and presented some guidelines for the prediction of detector sensitivity with respect to compounds unavailable in a pure form.

Calibration of katharometer becomes superfluous when the apparatus is fitted with a combustion chamber for elemental analysis filled consecutively with copper oxide and silver and which is placed between the column and the detector⁹². The sample components passing through this device are converted into hydrogen, which is registered by the detector. The appropriate calibration coefficients can be calculated theoretically on the basis of the hydrogen content of the component being analysed. This detector has been used in the analysis of polyorganosiloxanes⁹⁴, phenylchlorosilanes⁹³, phenylalkoxysilanes⁹⁴. Its application appears to be extremely advantageous, especially when standard compounds are not available, but its response is still slower than that of the katharometer and the degree of combustion of OSC must be determined in each instance.

The katharometer was shown to exhibit selective sensitivity towards organo-element compounds⁹⁵. For instance, the sensitivity to OSC was approximately 3-fold higher (6-fold to germanium and 9-fold to lead compounds) than to the carbon-containing analogues.

The use of flame-ionization detectors (FID) for OSC analysis is associated with various anomalies. Luskinia *et al.*⁹⁶ demonstrated that the sensitivity of the FID was dependent on the C:Si ratio in the sample. Pollard *et al.*²⁵ demonstrated that the FID is easily overloaded with OSC, which results in flattened peaks after reaching a certain threshold value of the sample volume. To avoid this, they recommended reducing the size of the sample or installing an effluent splitter between the detector and the column. Peak inversion was registered for OSC by Fritz *et al.*⁹⁷ using an FID. The intensity of the detector signal plotted against mass of silicon produced a curve with a maximum. The effect of gas flow through the detector on the above phenomenon was studied. Infusion of acetylene into the hydrogen flame caused complete inversion of OSC peaks, the magnitude of the observed effect being correlated with the C:Si ratio, which makes it applicable to the qualitative analysis of siloxanes. Background current can be attained in FID by adding methane^{98,99}. It has been suggested

that in this mode of operation negatively charged ions are generated by OSC, whereas positively charged ions in considerably smaller amounts are produced by organic compounds. Under normal operating conditions, the sensitivity of such a detector ranges from 80 to 200 nC per gram of silicon, and the lowest detectable amount is $1 \cdot 10^{-9}$ g/sec. The parameters of the detector were studied using an X-Y recorder by comparing the signal of a standard detector with that of the detector being studied¹⁰⁰. Selective features of the detector permitted its subsequent application for the quantitative analysis of the decomposition products of organosilicon polymers¹⁰¹.

The applicability of an alkali flame-ionization detector to the analysis of organo-element compounds was investigated by Dressler *et al.*¹⁰². They found it to be more sensitive to OSC than the ordinary flame-ionization detector. Also, it generated a positive signal in response to OSC, which did not occur with tin- and lead-containing compounds. The thermionic detector can be used for the analysis of HCl, COCl₂ and methyl- and ethylchlorosilane impurities in silicon tetrachloride¹⁰³.

Hill and Aue¹⁰⁴ proposed a flame-ionization detector operating in a hydrogen atmosphere as a selective detector for OSC. Its sensitivity to alkyl- and arylsilanes is 2-3-fold higher than that to hydrocarbons. The addition of small amounts of ferrocene to the flame causes inversion of OSC peaks and increases the sensitivity to these compounds by one order of magnitude. Although the mechanism of such selectivity is unknown, this detector may prove very useful for the analysis of OSC in the presence of a multi-component mixture of organic compounds. However, the detector possesses a comparatively low absolute sensitivity, of the order of tens of nanograms for tetramethylsilane.

To determine methylchlorosilanes, Garzo and co-workers¹⁰⁵⁻¹⁰⁷ used a cell in which the electrical conductivity of a hydrolysate was measured continuously.

An argon ionization detector has also been proposed for OSC analysis¹⁰⁸, but it appears to be unsuitable because of its extremely low sensitivity to OSC, which would decrease with the increasing chlorine content in the sample.

Fritz and Ksinsik¹⁰⁹ designed a device consisting of two flow-sensitive katharometer cells. The device resembles closely the gas density balance proposed by Martin and James¹¹⁰ and can be applied to quantitative analysis and molecular weight determinations with 5% accuracy. A similar detector was reported by Wurst^{111,112}. There have also been reports on ¹⁴C radioactivity detectors used for OSC analysis¹¹³. Selective OSC determinations can also be carried out using various spectral methods. The chromatograph can be connected with a flame emission or atomic-absorption spectrometer¹¹⁴⁻¹¹⁶. A UV detector¹¹⁷ permits the detection of impurities in OSC at the appropriate wavelength for each impurity.

Of the variety of detection systems used for the analysis of OSC and organic compounds, the katharometer and FID are the only detectors with a wide range of application, and the other systems may be advantageous only in more specific analytical determinations.

4. STUDY OF ORGANOSILICON COMPOUNDS BY GAS CHROMATOGRAPHY IN COMBINATION WITH OTHER METHODS

The general aspects of GC in conjunction with chemical reactions and spectral analysis have been the subject of numerous publications, which were summarized by

Berezkin¹¹⁸ and Èttre and McFadden¹¹⁹. In OSC chemistry, reaction gas chromatography is mainly applied to functional analysis¹²⁰.

The use of reaction GC to identify unknown compounds as chlorosilanes was reported by Palamarchuk *et al.*²¹. Chlorosilane absorption was performed in the upper section of the chromatographic column with solid potassium hydroxide on an INZ-600 support. The chlorosilanes were completely absorbed by the sorbent, and the absorbent layer involved in the reaction had no effect on the retention values.

Reaction GC is applicable to the analysis of substances that cannot be separated by conventional GC. Difficulty is experienced, for example, in applying the direct method to the determination of trace amounts of phenyltrichlorosilane in methylphenyldichlorosilane. A pre-column containing sodium fluorosilicate installed prior to the chromatographic column permits the conversion of chlorine-containing silanes to the appropriate fluoro analogues, which can be separated more readily^{70,121}. Reaction GC can also be useful for the determination of relative amounts of $(\text{CH}_3)_3\text{Si}-$, $(\text{CH}_3)_2\text{Si}=\text{}$ and $\text{CH}_3\text{Si}\equiv$ groups in methylsiloxane polymers. The procedure consists in decomposing the polymers with an ethereal solution of boron trifluoride¹²² or sodium bifluoride¹²³ in a closed system and with subsequent GLC analysis of the resulting methylfluorosilanes either on a capillary column coated with SE-30¹²² or on a column packed with fluorosilicone FS-16¹²³.

A reaction GC device designed for group determination in OSC through Si-C bond hydrolysis in C-halogenated compounds has been reported¹²⁴. The stability of Si-C bonds in β -trimethylsilylpropionic and β -dimethylbutylsilylpropionic acid towards sulphuric acid was determined by measuring methane and butane generated in the reaction¹²⁵. A simple micro-scale method for Si-H bond determination was described by Franc and Mikes¹²⁶, which involved decomposition of OSC on a moist mass impregnated with potassium hydroxide, the hydrogen evolved being accumulated in a syringe and its amount measured using an activated carbon column after completion of the reaction.

Several studies have dealt with the problem of vinyl group determination in siloxane polymers. Conversion of vinyl groups into ethylene can be achieved through reaction with 90% sulphuric acid¹²⁷ or phosphorus pentoxide^{128,129}, by polymer fusion with potassium hydroxide¹³⁰ and by pyrolysis¹³¹. The last procedure also permits the determination of alkoxy groups by measuring the yield of alcohols, both vinyl and alkoxy groups being detectable at the 0.1–0.01% level. Combined methods for the qualitative analysis of OSC by means of TLC with subsequent application of reaction GC have also been developed^{132,133}. In this instance the material from the thin-layer chromatograms is transferred into a micro-reactor to be further treated with boron trifluoride, followed by chromatographic analysis of the reaction products.

Franc and co-workers^{134–136} presented a systematic method for OSC analysis based on reaction GC. Detection of alkoxy and phenyl groups is carried out by reaction with boron tribromide; ethylene oxide and propylene oxide rings can be detected by measuring the acetaldehyde or propionaldehyde produced in the reaction of OSC with potassium hydrogen sulphite. Treatment with potassium persulphate allows the identification of C=C double bonds, whereas reaction with solid potassium hydroxide at 200° is employed for the determination of the terminal $-\text{Si}(\text{CH}_3)_3$ and $\equiv\text{SiC}_6\text{H}_5$ groups. Sulphur can be detected in OSC by measuring the output of sulphur dioxide following treatment with boron trifluoride. The presence of carbon

chains bonded to a silicon atom is revealed through catalytic conversion on aluminosilicate modified with tungsten and molybdenum oxides. Acetyl groups are determined by hydrolysis with subsequent analysis of acetic acid. Chromatographic parameters for the determination of volatile products have also been elaborated.

A systematic approach to the analysis of functional groups and some bond types in OSC was described by Franc and Dvoracek¹³⁷. The compounds to be analysed were decomposed in a micro-reactor using sulphuric acid, hydriodic acid, potassium hydroxide or other reactants and the volatile reaction products were passed through a chromatographic column. The procedure is applicable to alkyl, chloroalkyl, vinyl, alkoxy and phenyl groups and also to Si-Si and H-Si fragment determinations.

Thus, reaction gas chromatography offers fairly wide possibilities for the study of OSC. However, most reactions employed in OSC determinations are time consuming and require a very long time for their completion compared with peak elution from chromatographic columns. This advantage limits considerably the applicability of reaction GC to the analysis of multi-component mixtures.

GLC is inapplicable to the direct analysis of siloxane polymers. Nevertheless, some information about the properties of these substances can be obtained by determining the amounts and composition of some comparatively volatile impurities that can be detected by conventional GLC¹³⁸.

Gas chromatography-mass spectrometry has been applied to the identification and structural analysis of silsesquioxanes¹³⁹ and the analysis of the pyrolysis products of polydimethylsiloxanes^{61,140}. Reaction GC of OSC using preliminary fusion has been also studied¹⁴¹.

The method for the determination of trimethylsilyl groups in amino and carboxylic acid derivatives is based on the gas chromatographic analysis of trimethylphenoxysilane formed on exposure of the sample to phenol¹⁴².

A method of rapid stationary phase selection for siloxane resolution has been described¹⁴³ in which relative retention parameters are estimated as follows:

$$\log V_{rel} = E \Delta \nu_i^{ASS} + F \quad (21)$$

$$\Delta \nu_i^{ASS} = \nu_{i(\text{squalane})} - \nu_{i(\text{polar phase})} \quad (22)$$

where ν_i denotes the shift in Si-H stretching frequency, and E and F are constants.

GLC can also be used to measure the vapour pressure of OSC¹⁴⁴ and to choose potential separating agents for extractive distillation of methylchlorosilanes¹⁴⁵.

5. GAS CHROMATOGRAPHY OF ORGANOSILICON COMPOUNDS AND MIXTURES THEREOF

The conditions required for OSC analysis are summarized in Table I. Stationary phases of general usage, such as Apiezon and siloxane polymers characterized by low or medium polarity, are most frequently employed for the analyses. Only with alkylchlorosilanes more polar phases such as phthalates, nitrobenzene and tricresyl phosphate are used. The amount of stationary phase loaded is dependent primarily on the volatility of the sample components and ranges from 5 to 33%. Capil-

TABLE I
 CONDITIONS FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF ORGANOSILICON COMPOUNDS AND THEIR MIXTURES

Compounds	Composition of packing	Column dimensions [mm × mm or (ft. × in.)]	Column temperature ("C)	Reference
<i>Halogenosilanes</i>				
Volatile silanes	DC-702 on Celite			69
Chlorosilanes, methylchlorosilanes	SF-96, QF-1			246
Methylchlorosilanes, silicon tetrachloride	Nitrobenzene, dibutyl phthalate, α -chloronaphthalene on Termalite, Sterchamol, Celite	1600	27	107
Alkylchlorosilanes (impurities in SiCl ₄)	16% E-301 on Chromaton N AW HMDS			103
Methylchlorosilanes	10% dioctyl phthalate on Celite, 80-100 mesh		20-25	108
	Nitrobenzene (30%)	1300 × 4	25	247
	15% FS-16 on INZ-600	3000 × 4	40	146
	10% diethyl phthalate on Celite, 80-100 mesh			98
Methylchlorosilanes	Two columns in series: paraffin oil and insulator oil in firebrick	4000 × 5	50-70	147
	Tricresyl phosphate and dioctyl phthalate			148
	Diethyl phthalate and silicone DC-200/350 on Kieselguhr (60:20:100)	2400	60	149
	α -Chloronaphthalene, dibutyl phthalate, nitrobenzene on Celite, Sterchamol, Termolite			106
	20% nitrile silicone OE-4178		35	90
	Paraffin oil, insulator oil on C-22, 30-60 mesh			150
	15% FS-16 on INZ-600	3000 × 6	70	151
	Polydimethylsiloxane on silanized silica gel		230	152
	Benzophenone		52	153
Methylchlorosilanes (reaction mixture from synthesis)	In series: 15% PFMS-4 on Celite and 15% vaseline oil on Celite	1000 × 3.5	40	154
	20% PFMS-3	3000 × 4	40	154
	20% DC-701 on INZ-600	4000 × 4	40	154
Methyltrichlorosilane (purification from traces of P and metals)	20% DC-701 on INZ-600	3600 × 20	50	155
Methylchlorosilanes (impurities: POCl ₃ , PCl ₃)	Vaseline oil, siloxanes VKZL-94, DC-701, fluorosiloxane 169, dinonyl phthalate (20%)	1000 × 6	50	156
Methylchlorosilanes, phenylchlorosilanes, lower methylpolysiloxanes	Silicon gum, liquid paraffin			157
Methylchlorosilanes (analysis of impurities)	Dibutyl phthalate and tricresylphosphate on INZ-600	3000 × 4	40	158

Dimethyldichlorosilane (analysis of impurities)	20% VKZ-94 on INZ-600	70, 30	159
Methylchlorosilanes (high-boiling by-products)	Polymethylphenylsiloxane oil	130	160
Ethylchlorosilanes	15% FS-16 on INZ-600	80	21
Ethylchlorosilanes (reaction mixture from synthesis)	10% MSO-150	90	161
Ethylchlorosilanes (product of chlorination)	PFMS-4 on Celite 545, E-301 on TND-TSM	90	32
Alkylchlorosilanes, low-boiling	DC-200/350 and dibutyl phthalate on Kieselguhr (3:1:5)	95	32
Alkylchlorosilanes, high-boiling	Silicone on Kieselguhr (3:10)	30-60	162
Alkylchlorosilanes	Nitrotoluene, XF-1112, QF-1, SE-30 (15%) on silanized Chromosorb, 60-80 mesh	150	162
2- and 3-pentylchlorosilanes	Apiezon L on Chromosorb	2000 × 4	38
Chloroalkyltrichlorosilanes	15% PFMS-4 or 3% FS on silanized diatomite brick	2500	163
Tris- γ -trifluoropropylchlorosilane (analysis of impurities)	15% fluorosiloxane 169 on INZ-600	2000 × 4	164
Methoxy- and ethoxychlorosilanes	SE-30, FS-16, Carbowax 6000, Apiezon L, DC-550 on Rysorb or Chezasorb	1000 × 3	166
Diethoxymethylchlorosilane	Methylsiloxane oil (Perkin-Elmer C)	2000 × 4	167
Alkoxychlorosilanes	Apiezon, PMS-100, FS-16, DC-550 on Chezasorb, Apiezon 0.2-0.36 mm	1000 × 3	168
$[\text{Cl}_2\text{Si}(\text{OC}_m\text{H}_{2m+1})_n]_n$; $n = 1$ or 4, $m = 1-4$	Rysorb 0.2-0.36 mm	125	167
Alkoxychlorosilanes	Apiezon L, SE-30, FS-16 on silanized Chezasorb	1000 × 3	62
Phenylchlorosilanes	20% E-301 on Chromosorb	240	93
(reaction mixture from synthesis)	Polymethylphenylsiloxane on Rysorb BLK	210	117
Phenylchlorosilanes	15% FS-303 on INZ-600	130	146
Tolylphenylchlorosilanes	5% E-301 on Porovina	170, 197	169
Methylphenyldichlorosilane	10% PFMS-4 on INZ	170	170
(impurities of dimethylphenylchlorosilane and phenyltrichlorosilane)	20% SKTFT-50 on Celite 545	100	171
Vinylchlorosilane	Dibutyl phthalate and tricresylphosphate on INZ	3000 × 4	158
Vinylchlorosilanes,	Nitrobenzene on Kieselguhr (3:10)	1800 × 4	172
methylynylchlorosilanes,	Dibutyl phthalate on Celite	1600 × 5	105
Methylynylchlorosilane,	Nitrobenzene on Kieselguhr, silicone elastomer on Celite, Dibutyl phthalate on Rysorb BLK	40, 25	173
Methylynylchlorosilanes	SE-30	27	174
Alkenyldichlorosilanes	Apiezon L + polyphenyl ether	(9 × 3/8)	174
<i>cis-trans</i> isomers	Capillary		174

(Continued on p. 272)

TABLE I (continued)

Compounds	Composition of packing	Column dimensions (mm × mm or ft. × in.)	Column temperature (°C)	Reference
Methylfluorosilanes	SE-30 on capillary columns or squalane on Teflon 6			122
Phenylfluorosilanes, cycloalkylfluorosilanes	30% UCW-98 on Chromosorb W			121
Perfluorophenylsilane	SE-30 on Chromosorb W	(1.5 × 1/4)	150, 205	175
Phenylhalogenosilanes	Perkin-Elmer O	3000	100, 125	176
Ethoxyfluorosilanes	DC-200 or mixture of diethyl phthalate and silicone oil			177
	Apiezon, DC-550, FS-16, XE-60 (5%) on silanized Rysorb and			24
	Chetasorb (0.3–0.36 mm)		70–100	
<i>Alkoxysilanes</i>				
Methylethoxysilanes (deuterated) (preparative GC)	20% SKFT-50 on C-22	4800 × 17		178
Methylethoxysilanes	Apiezon L, linear siloxane polymer			108
Methyltriethoxysilane, chlorobenzene	2,4,7-Trinitrofluorenone on Chromosorb			181
Trimethylethoxysilane	Didecyl phthalate		75	179
Butoxyethoxysilanes	E-301 on Celite 545		170	180
Vinylethoxysilanes	E-301 or silicone 7100 on Chromosorb (20:100)	1450 × 5	150–240	56
Methylphenylethoxysilanes	Silicone elastomer on Chromosorb or Kieselguhr (20:100)	1450 × 5	175, 240	181
Diphenyl(methylethoxysilane, phenyl(diethoxy)methoxysilane <i>tert.</i> -Butylphenyldimethoxysilane	Silicone elastomer 7100		180	94
Phenylethoxysilanes (reaction mixture from synthesis)	Didecyl phthalate (Perkin-Elmer A)	2000		182
Trimethylalkoxysilanes	10% SE-30 on Chromosorb		160–310	185
Ethylpropylsilicates	15% SE-30 on Chromosorb W, 30–60 mesh	1000 × 6	82	55
Tetraalkoxysilanes, <i>tert.</i> -butyrialkoxysilanes	20% Triton X-100 on Chromosorb P, 60–80 mesh	(4 × 1/8)	80–160	183
Tetraethoxysilane (products of thermal degradation)	Didecyl phthalate (Perkin-Elmer A)	2000		182
Tetraalkoxysilanes and phenyltriethoxy- silane (products of reaction with <i>tert.</i> -butyl chloride)	4.14% polypropylene glycol on Chromosorb P, 45–60 mesh	1000 × 6	40	186
Alkoxysilanes	Didecyl phthalate	2000	115–165	182
	1% Apiezon L on Chromosorb W	(1 × 0.25)	60–150	40
	Apiezon L, QF-1, SE-30 (10%) on Chromosorb, 60–80 mesh	2000 × 4	60–240	38
		2000 × 2		

Alkoxysilanes, siloxanes	5% silicone elastomer on Chromosorb P	2000 × 4	134	184
Methylphenoxysilanes	Polydimethylsiloxane on silanized silica gel		230	152
Trimethylacetoxysilane	Diisodecyl phthalate		75	179
<i>Siloxanes</i>				
Hexamethyldisiloxane	Silicone		100	188
Hexamethyldisiloxane, technical grade	Dibutyl phthalate on Chromosorb A (2:10)		35	41
	Lucoptene 1000 on Chromosorb A (1:10)		120	41
	10% PMS-100 on silanized INZ-600		130-170	189
Dimethylololigosiloxanes (linear and branched)	20% SKTFT-50 on C-22	4800 × 17		190
Siloxanes (preparative GC)	20% SKTFT-50 on C-22	2000 × 14	200-220	191
Siloxanes, high-boiling (preparative GC)	UCW-98, Apiezon L, QF-1 on Chromosorb W (30%)			192
Organosiloxanes, polysiloxanes	20% SKTFT-50 on C-22	2100 × 14	200-220	193
Alkylhydrosiloxanes and amino alcohols (preparative GC of reaction products)	Apiezon L, SE-30, PMS-100 on silanized Chromosorb (10%)	2000 × 3	100-300	81
Methyl- and ethylcyclosiloxanes	23% of linear polydimethylsiloxane of mol.wt. 80,000 on Chromosorb W, 0.2-0.3 mm	3650 × 5.3		194
Octamethylcyclotrisiloxane (analysis of impurities)	20% DC-703 on Sterchamol	1600 × 8	125	195
Methylhydrocyclosiloxanes	20% SKTFT-50 on Celite 545	2700		73
Methyl(propyl)dimethylcyclosiloxanes	20% of siloxane on Celite			72
Methyl(propyl)dimethylcyclosiloxanes, methyl(trifluoropropyl)cyclosiloxanes	CKTFT-50 on Celite 545	1740 × 6	130-203	196
Trifluoropropyl(methyl)dimethyl- cyclosiloxanes	2% cyclohexanedimethanol succinate on silanized Gas-Chrom P/AW		150	197
2,6- <i>cis</i> -Diphenylhexamethylcyclotetra- siloxane	Dimethylsiloxane-carborane copolymer	3000 × 4	235	198
Methyl(phenyl)dimethylcyclosiloxanes	Apiezon L or silicone gum on Chromosorb	(2)		199
Methylphenylcyclosiloxanes (isomers)	Nitrilsiloxanes NPS-50DF and NPS-100DF			200
Alkyl-(<i>β</i> -cyanoethyl)cyclosiloxanes	10% PMS-100 or 12% 139-15 liquid on Chromaton N	1000 × 4	180-	201
	10% PMS-100 on silanized INZ-600	2000 × 4	390	
		1000 × 4	175-300	70
Oligodimethyl(methyl)dichlorophenyl) cyclosiloxanes	10% PMS-100 on silanized INZ-600	2000 × 4		
Non-geminal divinylhexamethylcyclo- tetrasiloxanes	33% triethylene glycol, saturated with silver nitrate, on Chromosorb P, 100-120 mesh	1500 × 4	65	202
Siloxanes in atmosphere of SkyLab	Emulphor ON-870 on capillary	(600 × 0.02)	Program	203
Trimethyltriphenylchlorosiloxane (analysis of impurities)	11.3% PMS-100 on Chromaton N AW HMDS (0.25-0.315 mm)	3000 × 4	277	204

(Continued on p. 274)

TABLE I (continued)

Compounds	Composition of packing	Column dimensions (mm × mm or (ft. × in.))	Column temperature (°C)	Reference
Siloxanes (b.p. range 400°)	PMS-100 on silanized INZ-600	250 × 2 1000 × 2	100-340	205
Polymethylsiloxanes (linear and cyclic, <i>n</i> = 15)	10% LP-122 on Chromosorb P, 60-80 mesh	610 × 6.4	50-350	206
Polydimethylsiloxanes	Lucoprene on Rysorb BLK (20:100), 0.2-0.4 mm	1700 × 4	150, 195	45, 173
[linear (<i>n</i> = 2-7) and cyclic (<i>n</i> = 3-8)]	Lucooil M on Celite 545 (1:10)	1900 × 4	190	46
Polydimethylsiloxanes (linear and cyclic)	Lucoprene on Rysorb BLK	Variable	150-185	43
Oligosiloxanes (preparative GC)	Percentage loading variable	Variable	Variable	207
Polymethylsiloxanes	9% diphenyldimethylsiloxane polymer on Chromosorb W	(2)	100-300	208
[linear and cyclic (<i>n</i> = 40)]	5% polydimethylsiloxane on INZ-600	1000	246	209
Methylphenylpolysiloxanes (<i>n</i> = 1-4)	SKTFT-50		175, 235	210
Polyethoxysiloxanes	Didecyl phthalate		100-150	187
Trimethylsilyloxymethylgermane	Apiezon L on Chromosorb W		254	213
Bis-trimethylsilyl sulphide				
<i>N</i> Containing organosilicon compounds				
N-Alkylcyclotrisilazanes	12% SE-30 on Celite	(4 × 1/4)	180	28
Silazanes and disilazanes	Silicone	(5)		214
<i>trans</i> -(N-Alkyl)hexamethylcyclotrisilazanes (products of redistribution reaction)	12% SE-30 on Chromosorb W	(6 × 1/4)	180	29
Silatrane	Apiezon L, OV-17, OV-225 on Gas-Chrom Q AW B W DMCS (5%)	2400 × 3	200	211
Cyclic siloxanes	Silicone gum rubber	(2)	100-250	212
Isocyanatosilanes	5% of silicone gum on Flaloport F			215
Bis(trimethylsilyl)acetamide	OV-101, SE-30			216
<i>Organysilanes</i>				
Methylsilanes	25% of nitrodiphenyl on Embacel	(4)	40	217
Dimethylsilyl- and trimethylsilyl- substituted methane, ethane and ethylene	Polypropylene glycol (Perkin-Elmer R)	8500	150	218
Silane, methylsilanes	Tetraisobutylene		30	219
Tetramethylsilane	Apiezon	(8)		95

Ethylsilanes and other compounds of Group IVB elements	20% Apiezon L or 15% Carbowax 20M on Chromosorb W	1000 × 3	120	48
Isopropyl- and isobutylsilanes (sterically hindered)	15% E-301 on Silocel, 36-60 mesh	2000 × 5		30
Hexyltrimethylsilanes	Liquid paraffin NF on capillary	(183 × 0.02)	40	220
Alkylsilanes	Apiezon L on Chromosorb W	(5 × 0.5)		221
	13% Squalane on Embacel, 60-80 mesh			79
	Didecyl phthalate	2000	30	219
Alkylsilanes, -stannanes, -germanes	E-301		80-140	25
Trimethylheptafluoroisopropylsilane	Silicone elastomer		134	222
Di(trimethylsilyl)alkanes and -alkenes	Polypropylene glycol (Perkin-Elmer R)	6000	150	223
α,ω -Di(trimethylsilyl)alkanes	Polymethylphenylsiloxane oil			74
Dichlorosilyltrichlorosilylmethane, bistrichlorosilylmethane	Silicone C 200/350 on Kieselguhr 1200 (20:100)	1200	150	149
Triethylvinylsilane	Silicone gum (5%)			224
Vinyl- and allylsilanes	PFMS on INZ (20:100); Polyethylene glycol 1500 on INZ (20:100)	2000 × 6	125-175	75
Stereoisomers of Si and Ge derivatives of ethylene	GSC on graphitized carbon black, Apiezon L on Chromosorb W	1000	100-200	225
<i>cis</i> - and <i>trans</i> -1-trimethylsilylhexene-1	Apiezon L on Chromosorb	2500	200	163
Products of hydrosilylation of: hexene-1 and styrene	18% FS-1265 or 14.6% E-302 on Chromaton N	4000 × 4 2000 × 4	105-170	226
phenylalkenes	23% DC-200 on Chromosorb	(4 or 10)		227
hexene-1	23% QF-1 on Chromosorb P	(15 × 1/4)		228
	25% SF-96 on Chromosorb P	(5 × 1/4)		
alkynes	10% PEG 10000 on TND		180	229, 230
monosubstituted acetylenes	10% PEG 10000 on TND, 15% 1,2,3-tris-(β -cyanoethoxy) propane on Chromosorb W		130-180	231
Products of pyrolysis of phenyl-dimethylsilane	20% Apiezon L, 20% E-301, Apiezon L + Bentone 34 on Celite 545	1050, 2000	250	232
Chlorophenyltrimethylsilanes	7.5% Apiezon L + 7.5% Bentone 34	1800	120	233, 234
Chlorobenzylsilanes	10% Apiezon L, E-302	1100	150	
Triethylsilylethanol, triarylsilylethanol	Silicone gum (5%)	(3)		224
Products of silylation of polyalcohols	13% polysebacinate on Teflon		110, 155	235

(Continued on p. 276)

TABLE 1 (continued)

<i>Compounds</i>	<i>Composition of packing</i>	<i>Column dimensions</i> [mm × mm or (ft. × in.)]	<i>Column</i> <i>temperature</i>	<i>Reference</i>
Products of synthesis of 1,4'-bis(dimethylsilyl)benzene	5% poly-(4-dimethylsilyl-4-dimethylsiloxyphenyleneoxide) on INZ-600	6000 × 4	140	236
Sterically hindered Si-containing phenols and products of their oxydation	Apiezon L, E-301, Carbowax 20M, OV-17 on Chromosorb W		200	237
Bis(dialkylsilyl)arenes, arylsilanes	5% Arylenesiloxane elastomer	6000	141-146	243
Organosilicon derivatives of piperidine, pyrrolidine and perhydroazepine	Apiezon M, Carbowax 20M (20%) on Chromosorb W AW DMCS	3000 × 2	130	52, 53
2-Furylsilanes, germanes, stannanes, plumbanes	Apiezon L, Versamid 900, Carbowax 20M (10%) on Chromosorb W AW DMCS	2400 × 2.2	180	54
Si-substituted thiophenes	GSC on Spherochrom-I, 10% Apiezon L on Chromosorb W, 10% Reoplex 400 on Chromosorb W	1000 × 4		49
1,1-Dimethylsilacycloalkanes	Polymethylphenylsiloxane oil, polyethylene glycol 1540			74
products of dehydrogenation	20% PFM on INZ	2000 × 6	120	238
products of chlorination	Silicone TK-055	1800	130	239
	Silicone	5000	135	240
		(5)		241
Silacycloalkanes	Polypropylene glycol on Celite 545, SE-52 on Celite 545	9600 × 8	160-250	242
Hexaethylidisilane, triethyl(triethylsilyl)germanium	GSC on graphitized carbon black, Apiezon L and Carbowax 20M on Chromosorb W		150-250	50
	20% UCW-95 on Chromosorb W	2440 × 16	50-200	244

lary columns are seldom used. There are no special requirements for the carrier gases, except for chlorosilane analysis, when they have to be thoroughly dried. Undoubtedly, many of the stationary phases proposed by different investigators have very similar properties. Valuable information on their interchangeability is given in refs. 1 and 245.

6. SUMMARY

The present review deals with some problems that may be of interest to chromatographers studying organosilicon compounds (OSC). It is shown that correlations between structure and retention values of OSC help to predict retention parameters of unexplored compounds and help to gain insight into the physico-chemical processes in the gas chromatography of OSC. The detectors used for OSC analysis are discussed. A combination of gas chromatography with other methods is shown to be useful in functional group analysis as well as in the identification of separated compounds. The conditions of 160 analytical methods are tabulated.

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