

CHROM. 367I

CERTAIN REGULARITIES IN THE RETENTION OF CHLORINE-CONTAINING INORGANIC AND ORGANOMETALLIC COMPOUNDS

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SUMMARY

It was found that for some inorganic compounds there is a certain regularity in their retention behaviour when chromatographed on different stationary phases.

An investigation was made of the separation of volatile metal chlorides and some organometallic compounds having boiling points up to 250°. Based on the retention characteristics for a series of stationary phases, certain regularities have been analyzed which show a relationship between the retention volume and the physico-chemical properties of the stationary phases and the analyzed compounds.

Despite progress made in arriving at a theory of separation, separation conditions are often selected experimentally, the selection sometimes requiring a great number of experiments. In the case of halogen-containing inorganic and organometallic compounds, the difficulties arise from the lack of systematic investigations on the composition of the sample *versus* output characteristics, such as has been carried out to a considerable extent for hydrocarbons. Thus it is of interest to establish the relationship between the retention characteristics and the properties of the halogen-containing inorganic and organometallic compounds.

The separation of the investigated compounds was carried out on a chromatograph with a hot wire detector equipped with Teflon-coated tungsten coils and a pneumatic device for the injection of hydrolyzable samples¹, and a Teflon column 4 mm in diameter and 1.8 m long.

A type of Teflon, "Polychrom" (ref. 2), served as support. Based on known data^{3,4} we used the following stationary phases: siloxane elastomer E 301 ($E^* = 2.9$); Apiezon-N ($E = 2.65$); *n*-octadecane ($E = 2.15$); polyorganosiloxane liquid VKZh-94 ($E = 2.5$); liquid polytrifluorochloroethylene of the Kel F-10 type ($E = 2.6$); Kel F-3 and AlBr₃ ($E = 3.88$).

The results were analyzed according to the generally accepted concepts regarding specific retention volume, height equivalent of the theoretical plate, selectivity coefficient, and separation coefficient. The best results were obtained in the case of stationary phases consisting of polytrifluorochloroethylene, Kel F-3 and *n*-octadecane

* $E =$ Dielectric constant of the stationary phase.

(for example, the height equivalent of the theoretical plate for GeCl_4 on *n*-octadecane was 1.3 mm).

A plot was obtained for the dependence of the logarithm of the retention volume of silicon tetrachloride, germanium tetrachloride, tin tetrachloride, and titanium tetrachloride for a stationary phase (polytrifluorochloroethylene) *versus* the logarithm of the retention volumes of the same compounds on other stationary phases. The dependences obtained in Fig. 1 can be used in identifying inorganic chlorides according to known retention volumes on two or more stationary phases.

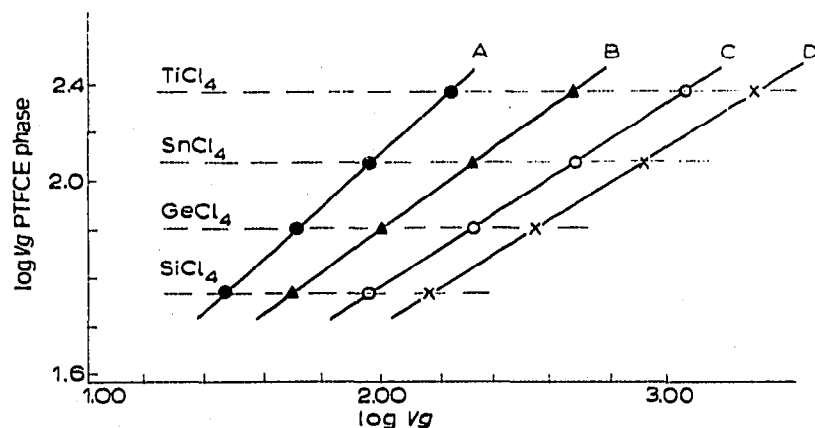


Fig. 1. Dependence of the retention volume of silicon tetrachloride, germanium tetrachloride, titanium tetrachloride *versus* the logarithm of the retention volume of the same compounds separated on other types of stationary phase. A = AlBr_3 melt; B = VKZh-94; C = Kel F-3; D = *n*-octadecane. The Teflon column was 1.8 m long and 4 mm in diameter using polytrifluorochloroethylene (PTFCE) as the stationary phase (5%) on a Teflon support. Temperature of the column: 80° . Carrier gas: He; flow rate of carrier gas: $26.6 \text{ cm}^3/\text{min}$; detector: katharometer.

According to theory, the dependence of the logarithm of the retention volume on the reciprocal of the dielectric constant of the stationary phase must be linear, while the slope of the straight lines depends on the nature of the substance being analyzed⁵. The relationships shown in Fig. 2 indicate that one can determine with sufficient precision the linear relation between the logarithm of the retention volume for some metal chlorides and the reciprocal of the dielectric permeability of the phases, the slope of the straight lines varying with the change in the polarity of the substances being analyzed (*e.g.*, in the case of SiCl_4 and PCl_3). Since the dielectric constant is not directly related to the parameters of the chromatographic experiment, the plotting of such relationships makes it possible to predict to a certain degree the magnitude of retention for the investigated compounds on new stationary phases.

The plot of the logarithm of the retention volume *versus* the boiling point of the compounds separated on polychlorotrifluoroethylene substrate also gives linear dependences (Fig. 3).

Since the straight lines have different slopes, characterizing different groups of compounds, it is clear that the dependence is not limited to the boiling points of the compounds, but includes the number of halogen atoms and the presence of other atoms (*e.g.*, O and S) attached to the metal. In this case a significant effect is also exerted by the different polarities of these compounds (the dipole moments of silicon tetrachloride, phosphorus trichloride and phosphorus oxychloride being 0, 0.78, 2.40

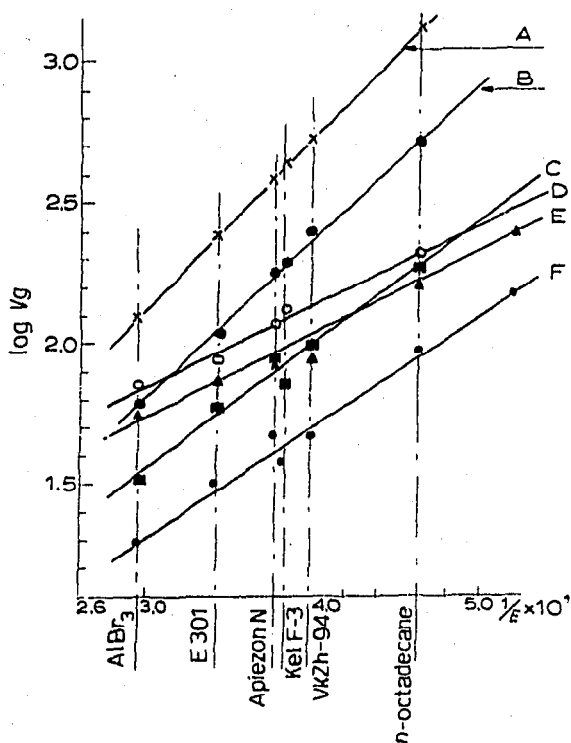


Fig. 2. Dependence of the retention volume of chlorine-containing compounds on the reciprocal of the dielectric permeability for some stationary phases. Experimental conditions as described in Fig. 1. A = TiCl_4 ; B = SnCl_4 ; C = GeCl_4 ; D = POCl_3 ; E = PCl_3 ; F = SiCl_4 .

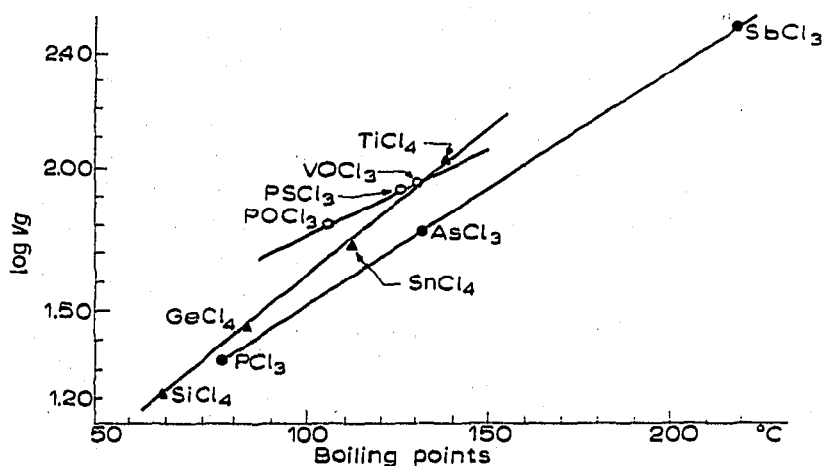


Fig. 3. Dependence of the logarithm of the retention volume on the boiling point of the metal chlorides. Experimental conditions as described in Fig. 1.

Debye units respectively). Owing certain differences in retention volumes, the investigated inorganic and organometallic compounds can be divided into three groups: nonpolar compounds (SiCl_4), compounds having a medium polarity (PCl_3), and polar compounds (POCl_3).

As is known, the solubility in nonpolar solvents (*i.e.*, in the stationary phase) is determined by the dispersion forces which depend on the polarizability (α) or molecular

refraction (R). It has already been shown⁶ that for a homologous series of hydrocarbons there is a linear dependence of the logarithm of retention volume on the molecular refraction of the analyzed compounds in the case of nonpolar solvents. In the case of nonpolar molecules, such as the compounds of the first group (MR_4): $\alpha_{atomic} = 0$ and $\alpha_{orientational} = 0$ (here, $M = \text{metal}$); the molar refraction (R_D) here is an approximate indication of the electron polarizability of the molecule.

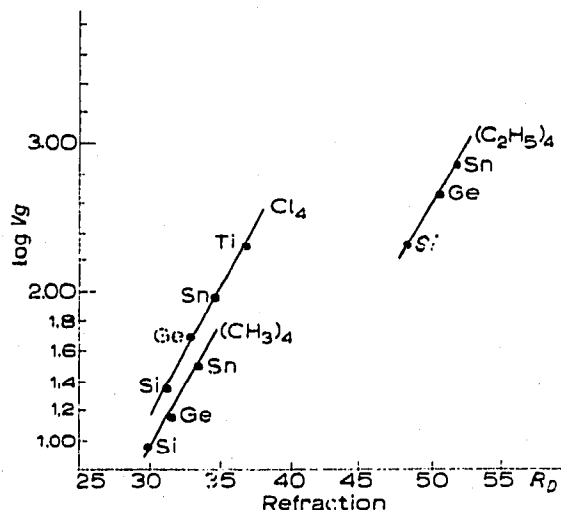


Fig. 4. Dependence of the logarithm of retention volume of some of the investigated compounds on the molar refraction of the same compounds using polytrifluorochloroethylene as the stationary phase (5%) on a Teflon support at 80° . The remaining experimental conditions as described in Fig. 1.

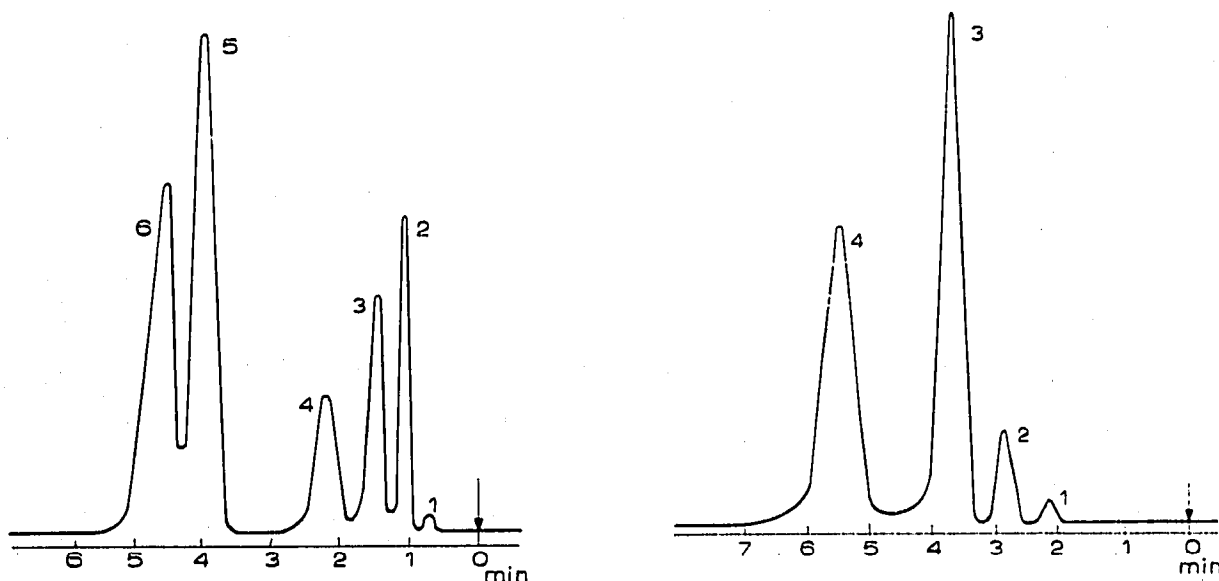


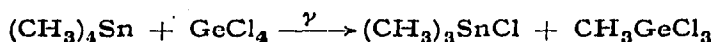
Fig. 5. Chromatogram obtained during the separation of titanium tetrachloride from vanadium oxychloride using polytrifluorochloroethylene as the stationary phase (5%) on a Teflon support at 80° . 1 = HCl; 2 = SiCl_4 ; 3 = GeCl_4 ; 4 = SnCl_4 ; 5 = VOCl_3 ; 6 = TiCl_4 .

Fig. 6. Chromatogram of the reaction products of germanium tetrachloride and tetramethyltin using *n*-octadecane as the stationary phase (20%) on a Teflon support ("Polychrom") at 120° . 1 = $(\text{CH}_3)_4\text{Sn}$; 2 = GeCl_4 ; 3 = $(\text{CH}_3)\text{GeCl}_3$; 4 = $(\text{CH}_3)_3\text{SnCl}$.

The plot of the logarithm of the retention volume *versus* their molar refraction (Fig. 5) for the compounds being separated on *n*-octadecane as the stationary phase is linear in nature. The relationships obtained were used in the analysis of mixtures of chlorine-containing inorganic and organometallic compounds.

One of the most undesirable impurities contained in technical grade titanium tetrachloride is vanadium oxychloride, which has approximately the same boiling point as titanium chloride. Owing to a small partition coefficient difference it is impossible to achieve the complete separation of VOCl_3 from TiCl_4 by means of distillation. A chromatogram (Fig. 5) shows the presence of impurities in TiCl_4 .

The study of the synthesis of chlorine derivatives of tin and organogermanium compounds by the reaction of tin tetraalkyls with germanium tetrachloride in the presence of γ -radiation from a ^{60}Co source⁷ showed (Fig. 6) that the reaction proceeds according to the scheme:



The yield of methyltrichlorogermanium in this reaction based on chromatographic analysis is 96%. The relationships between the logarithm of the retention volume and the boiling point of the corresponding compounds is used for the identification of the compounds. The mixed chloro- and alkyl-derivatives show a linear dependence having a different slope from that for tetrachloro- and tetraalkyl-derivatives (Fig. 7).

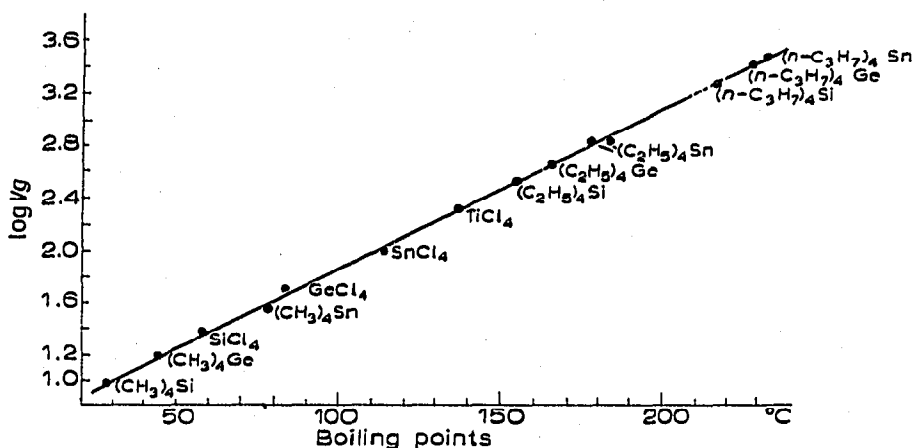


Fig. 7. Dependence of the logarithm of the retention volume on the boiling point of the investigated compounds. Column length: 2 m; column diameter: 3 mm; column temperature: 120°. The column is made of Teflon and filled with 20% of *n*-octadecane on a Teflon support "Polychrom".

The results obtained indicate that the retention data for this group of compounds conform to the same regularities as those for hydrocarbons⁶. The data obtained for the retention volumes for different stationary phases make it possible to predict the conditions for the separation of other mixtures containing the investigated compounds. The dependences obtained should only be considered as a first approximation towards the solution of the problem under discussion, which nevertheless is useful in the analysis of retention data and in designing separation schemes for the analysis of volatile metal compounds.

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