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ISOLATION OF SOME HIGH-BOILING ORGANOMETALLIC COMPOUNDS BY PREPARATIVE GAS CHROMATOGRAPHY*

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Preparative gas chromatography is proposed to isolate some high-boiling organometallic compounds. Isolation of high-boiling substances should be conducted at a column temperature significantly below the boiling point, because most isolated compounds are thermally unstable at such temperatures. Stationary phases for preparative gas chromatography have a temperature limit of 350°C. The reduction of the column temperature is based on simultaneous changing the parameters of the chromatographic experiment (column length, impregnation degree, flow rate of the carrier gas). The influence of reducing the column temperature on the shape of the chromatographic peak is shown. The peak has an asymmetric shape, and its width increases. Therefore, the possibility of high-boiling substances preparative isolation depends on temperature decrease as the column separation efficiency is maintained.

Keywords: *preparative gas chromatography, organometallic compounds.*

Introduction

Up to this day isolation of high-boiling substances, such as oils for diffusion pumps, thermally unstable compounds, is carried out by vacuum distillation, short-path distillation. The latter method is used for isolating thermally unstable substances and compounds with molecular weight up to 1400 Da. Seemingly, this sphere should be completely covered by high-performance liquid chromatography (HPLC). However, as seen by the example of some polyorganosiloxanes, the selectivity of liquid chromatography [1, 2] is lower than that of gas chromatography. Perhaps, the ability of predicting regularities of chromatographic retention for molecules of different structure and for sorbents of different type will allow increasing HPLC selectivity [3].

The maximum temperature of gas-chromatographic separation depends on the thermal stability of the stationary phases. The literature presents a broad scattering of data (370–480°C) by the maximum permissible working temperature of the most heat-resistant organosilicon phases [4, 5]. At the same time it is shown in monograph [6] on thermal degradation of polyorganosiloxanes that Si–C bond is stable up to the temperature 350°C, above which elimination of organic radicals is observed.

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Substances isolated by short-path distillation are successfully separated by the gas-chromatography method of isolation of high-boiling substances at low temperature [7]. The partial pressure of these substances at the analysis temperature is about 1 mm Hg. Reduction of partial pressure is accompanied by a deviation of the distribution isotherm from linearity and a significant increase in the width of the chromatographic peak. Seemingly, it makes impossible using this method in preparative chromatography, where concentrations of substances separated in a column are much higher. However, choosing the optimal conditions of chromatographic separation enables obtaining rather good results.

The purpose of this work is to choose the optimal conditions of chromatographic separation of some high-boiling organoelement compounds (see the table) by preparative gas chromatography.

Experimental

Analysis of the original mixture and determination of the purity of isolated compounds were carried out with the use of LKhM-7A and TsVET-530 chromatographs with a heat conductivity detector. The isolation was carried out with the use of PAKhV-07 preparative gas chromatograph produced by special design bureau INHS. A column 1 or 2 m long with a diameter from 14 to 24 mm was filled with a sorbent by means of a vibrator. The columns were filled with a ready sorbent Chromatone N AW with 5% of SE-30. Separate portions of the sorbent were prepared in a porcelain cup by evaporation in 20 g portions. 15% polymethyl-γ-trifluoropropylsiloxane liquid FS-303 was applied on the solid carrier Chromatone N AW. 14% of polymethylphenylsiloxane liquid PFMS-6 was applied on a INZ-600 brick treated by dimethyldichlorosilane vapor. This sorbent was kept at 400°C during 24 h. After this the remaining amount of PFMS-6 liquid was 6.8%. The obtained sorbent could work a long time at 350°C. The high boiling temperature of some of these compounds results in the formation of a steady aerosol. So, the most part of the pure substance is carried away from the trap upon condensation. In order to destroy the aerosol we used electrodeposition. The glass trap was wrapped up with copper foil. Voltage from a high-voltage inductor IV 100 was applied on the trap. The volume rate of the carrier gas was limited by the extent of trapping of the collected compound. The maximal volume rate was determined separately for each mixture and changed from 0.7 to 1.5 l/min. This range of rates did not allow using columns with a diameter more than 24 mm.

Results and Discussion

Using the known relation of retention volume, column temperature, analysis time and the carrier gas speed we expressed dissolution heat in terms of boiling temperature according to Trouton's rule and obtained the following equation [7]:

$$4.6\frac{T_K}{T} = \lg\frac{u}{W} + \lg\tau + C\,, \qquad (1)$$

where T is the column temperature; T_b is the analyte boiling temperature; u is the linear velocity of the carrier gas; W is the amount of the stationary phase per unit of sectional area ($W = L \cdot \delta \cdot \rho$); L is the column length; δ is the thickness of the stationary phase layer; τ is retention time; ρ is the liquid phase density; C is a constant.

The main criterion of preparative chromatography is productivity. Productivity (P) depends on the sample volume (V), initial concentration of a component in the mixture (C_o), cycle time (τ) (that is, the interval of time, after which the sample is repeatedly entered into the chromatograph), selection coefficient (C_s) and coefficient of catching ($C_c = K_y$).

Evaluation of the quality of the chosen conditions for each mixture can be carried out on the basis of the values given in the table.

PFMS-5 liquid produced by the Russian industry [8] is used as a stationary phase for gas chromatography. It is a polydispersed mixture of ω,ω'-dimethyltetraphenyloligo-methylphenylsiloxanes. A number of fractions were obtained from this liquid by short-path distillation. Preparative isolation of individual compounds was carried out from such fraction on a PAKhV-07 chromatograph (Figure 1). The formulas of these compounds are given in the table at Nos. 1 and 2.

The boiling temperatures of these compounds are, respectively 543 and 590°C. So, evaporator temperature 600°C was chosen. The carrier gas speed was 1.5 l/min. Condensation of these high-boiling substances occurs to catching coefficient up to 70%. This value can be increased to 80% by reducing the carrier gas speed to 0.5–0.7 l/min, but this leads to reduction of productivity. The purity of the isolated compounds was 99%.

Introduction of the thionyl substituent at the silicon atom of an oligoorganosiloxane improves its lubricating properties [8]. The boiling temperatures of methylthienylcyclotri-, tetra- and pentasiloxane are a little lower than those of the corresponding methylphenyl-cyclosiloxanes. Nevertheless, the boiling temperature of methylthienylcyclopentasiloxane exceeds 500°C.

Parameters of isolation of some high-boiling organoelement compounds by preparative gas chromatography

Compound number	Compound	Sample volume, V, ml	Productivity, P, ml/h	Selection coefficient, C_s	Coefficient of catching C_c (K_y)	Cycle time τ, min	Concentration of the substance in the mixture, C_0,%
1	$CH_3(C_6H_5)_2Si[O(CH_3)(C_6H_5)Si]_2(C_6H_5)_2CH_3$	1.0	0.96	0.80	0.70	15	0.43
2	$CH_3(C_6H_5)_2Si[O(CH_3)(C_6H_5)Si]_3(C_6H_5)_2CH_3$	1.0	1.15	0.75	0.70	15	0.55
3	$[O(CH_3)(C_4H_3S)Si]_3$	1.0	0.34	0.85	0.80	24	0.20
4	$[O(CH_3)(C_4H_3S)Si]_4$	1.0	0.83	0.80	0.80	24	0.52
5	$[O(CH_3)(C_4H_3S)Si]_5$	1.0	0.49	0.90	0.80	24	0.27
6	$[(C_8H_{17}O)_2CH_3SiC_5H_4]_2Fe$	0.30	0.32	0.70	0.80	24	0.76
7	$P_3N_3Cl_2(OR)_4$*	0.25	0.06	0.78	0.48	24	0.25
8	$P_3N_3Cl(OR)_5$*	0.25	0.25	0.76	0.80	24	0.66
9	$P_3N_3(OR)_6$*	0.25	0.02	0.80	0.45	24	0.08
10	Hexyl-*o*-carborane	0.50	1.16	0.64	0.95	15	0.96

*R – $CH_2CF_2CF_2H$

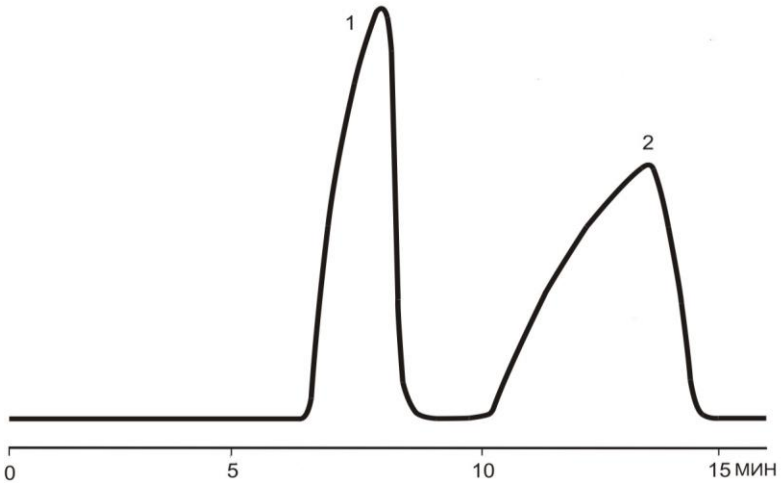

Figure 1. Chromatogram of preparative separation of a mixture of ω,ω'-dimethyltetraphenyl(methylphenyl)tetra- and pentasiloxanes. Column length: 1 m, diameter: 24 mm. Sorbent: 6.8% PFMS-6 on INZ-600 DMDCS. Column temperature: 350°C.
[here and below: мин means min]

When choosing conditions for the isolation of these compounds (Nos. 3, 4 and 5 in the table), methylsilicon rubber SE-30 on Chromatone N AW and the stationary phases PFMS-6 and PMS-100 on INZ-600 treated with dimethydichlorosilane were used. The sorbent with 5% of SE-30 on Chromatone N AW (Figure 2) was chosen, because strong adhesion was observed upon isolation of these compounds on INZ-600. As a result, the isolated substance used to contain 1–2% of impurities of other methylthienylcyclosiloxanes.

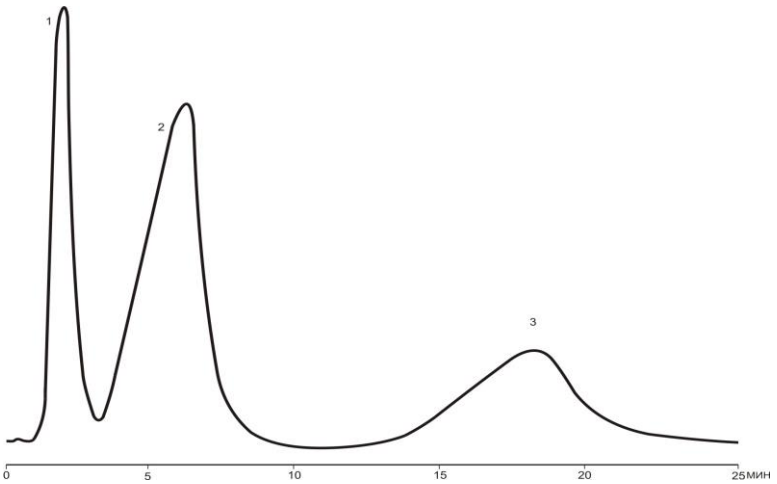

Figure 2. Chromatogram of preparative separation of methylthienylcyclosiloxanes: 1 – $[O(CH_3)(C_4H_3S)Si]_3$; 2 – $[O(CH_3)(C_4H_3S)Si]_4$; 3 – $[O(CH_3)(C_4H_3S)Si]_5$. Column length: 1 m, diameter: 24 mm. Sorbent: 5% SE-30 on Chromatone N AW. Column temperature: 300°C. Carrier gas speed: 1.0 l/min.

When isolating methylthienylcyclosiloxanes, the main part of the substance is carried away from the trap with the formed aerosol. Using electrodeposition allowed to increase catching coefficient up to 80%. The purity of the isolated compounds was 99%.

The unique properties of alkyl derivatives of ferrocenes give broad potentials of their application in technology. These compounds have high boiling temperatures, but many of them are thermally unstable at such temperatures.

The boiling temperature of 1,1'-bis (methyldioctoxysilyl)ferrocene (compound No 6 in the table) is 538°C. It can be seen from the chromatogram of preparative separation of 1,1'-bis (methyldioctoxysilyl)ferrocene presented in Figure 3 that isolation time at column temperature 300°C is about 25 min.

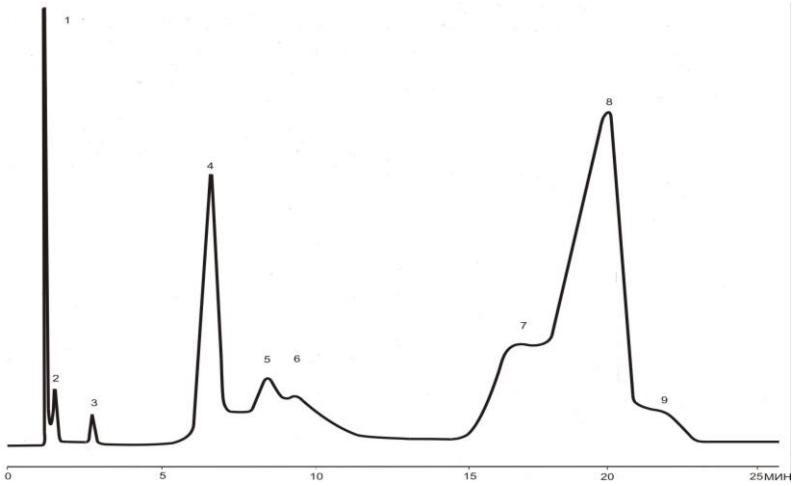

Figure 3. Chromatogram of preparative separation of 1,1'-bis (methyldioctoxysilyl)ferrocene:
1 – solvent; 2, 3, 4, 5, 6, 7, 9 – unknown impurities; 8 – target compound.
Column length: 1 m, diameter: 14 mm. Sorbent: 5% SE-30 on Chromatone N AW. Column temperature: 300°C.

In order to reduce isolation time, it was necessary to increase the carrier gas speed. However, catching coefficient abruptly fell at a speed higher than 0.8 l/min. Therefore, the column diameter 14 mm was chosen. The evaporator temperature was chosen to be 450°C. This temperature is low for a substance with boiling temperature 538°C, but at this temperature there were no decomposition products in the isolated substance. Nevertheless, a small amount of solid products accumulated in the evaporator, which resulted in the necessity of its mechanical cleaning. The low temperature of the evaporator did not allow increasing the sample volume to more than 0.3 ml. The purity of the isolated compound was 99%.

We did not succeed in separating by rectification chlorocyclophosphazenes, in which a part of the chlorine atoms is substituted by fluoroalkoxy groups, although these compounds considerably differ on boiling temperatures. Thus, $P_3N_3Cl_2(OCH_2CF_2CF_2H)_4$ (No. 7 in the table) has a boiling temperature of 355°C, $P_3N_3Cl(OCH_2CF_2CF_2H)_5$ (No. 8) – 374°C, and $P_3N_3(OCH_2CF_2CF_2H)_6$ (No. 9) – 412°C.

We found that mixtures of these chlorocyclophosphazenes are rather difficult to separate on the methylsilicone stationary phases (SE-30 and PMS-100) and on the polymethylphenylsiloxane stationary phase PFMS-4. However, these compounds are well

separated on fluorosilicone liquid FS-303. Figure 4 shows a chromatogram of a mixture obtained after separation on a preparative column.

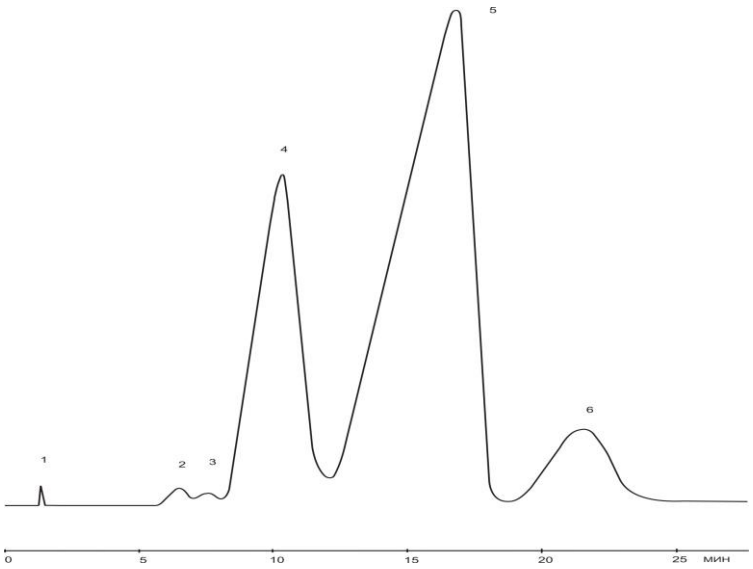

Figure 4. Chromatogram of preparative separation of fluoroalcoxychlorocyclotriphosphazenes:
1 – inlet reaction; 2, 3 – unknown impurities; 4 – $P_3N_3Cl_2(OCH_2CF_2CF_2H)_4$;
5 – $P_3N_3Cl(OCH_2CF_2CF_2H)_5$; 6 – $P_3N_3(OCH_2CF_2CF_2H)_6$.
Column length: 1 m, diameter: 24 mm. Sorbent: Chromatone N AW with 15% of FS-303.

The isolation was carried out at column temperature 235°C and the carrier gas speed 0.8 l/min. The sample volume was 0.25 ml. When increasing the sample volume, "overload" was observed, and the separation dramatically worsened. The retention time of the last component was 25 min. Reducing retention time can be attained by increasing the column temperature and the carrier gas speed. Unfortunately, the column temperature increase above 235°C is limited by its thermal stability [5], and the increase in the carrier gas speed results in a considerable fall of coefficient of catching and in losses of the isolated substances. The purity of the isolated compounds was 99%.

The isolation of some alkyl derivatives of carboranes was carried out for the purpose of determining their thermodynamic characteristics. A concentration of the main component not lower than 99.99% was required (or, otherwise, the total impurity level was required to be not higher than 0.01%). The isolation of hexyl-*o*-carborane was carried out from concentrates obtained by rectification. The concentrate contained 96% of the isolated substance.

When isolating this compound, adsorption on the surface of the solid carrier is of particular importance. Chromatone N AW impregnated with 5% of SE-30 was chosen as a sorbent. It was shown above that this solid carrier meets the specified requirements.

The preparative isolation was carried out at 225°C (Figure 5).

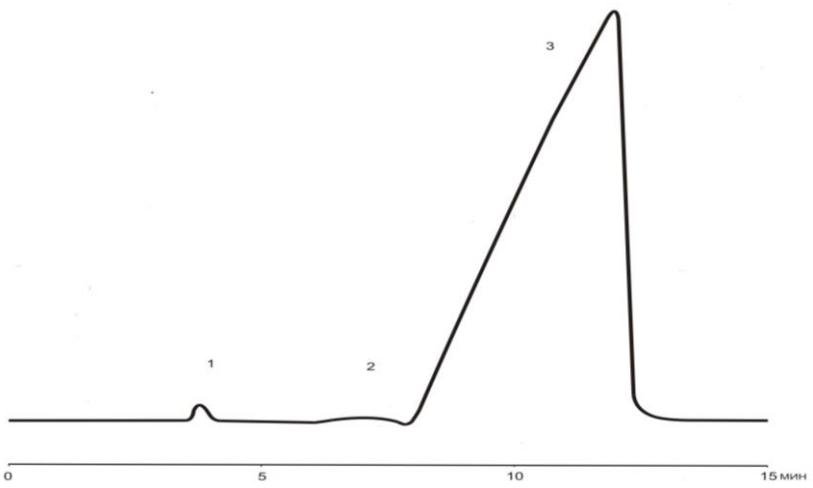

Figure 5. chromatogram of preparative isolation of hexyl-*o*-carborane:
1, 2 – unknown impurities; 3 – hexyl-*o*-carborane.
Column length: 1 m, diameter: 24 mm. Sorbent: 5% of SE-30 on Chromatone N AW.

However, in these conditions we succeeded in attaining 99.96% purity. This is accounted for by the fact that impurities were accumulated in the column and displaced from the sorbent surface by hexyl-*o*-carborane.

Using a column with a high content of another stationary phase (15% of PMS-100 on Chromatone N AW) upon simultaneous increase of the column temperature to 280°C did not give a positive result.

In order to reduce the amount of the sorbed substance we kept the column at 300°C for 2 h at the end of every day. Besides, the column was washed by the solvent after each inlet of hexyl-*o*-carborane. Acetone, benzene and toluene were tested as solvents. Using benzene and toluene led to a loss of the column efficiency. Thus, we chose acetone. After each inlet of a sample of hexyl-*o*-carborane acetone (0.5 ml) was added. All this allowed obtaining hexyl-*o*-carborane of 99.99% purity.

When isolating hexyl-*o*-carborane, an aerosol is formed, so, electrodeposition was used. When the carrier gas speed was 0.8 l/min, the coefficient of catching was 90%.

Thus, the possibility of isolating high-boiling substances by preparative gas chromatography was shown.

References:

1. Turkel'taub G.N., Chernyshev E.A. // Sorbcionnye i khromatograficheskie processy (Sorption and Chromatographic Processes). 2005. V. 5. № 3. P. 313–318. (in Russ.).
2. Turkel'taub G.N., Polyakova V.S., Chernyshev E.A. // Sorbcionnye i khromatograficheskie processy (Sorption and Chromatographic Processes). 2012. V. 12. № 2. P. 185–188. (in Russ.).
3. Belyakova L.D., Buryak A.K., Larionov O.G. // Fizikokhimiya poverkhnosti i zashchita materialov (Protection of Metals and Physical Chemistry of Surfaces). 2013. V. 49. № 6. P. 551–574. (in Russ.).
4. Yashin YA.I., Yashin E.YA., Yashin A.Ya. Gazovaya khromatografiya (Gas Chromatography). M.: TransLit Publ., 2009. 528 p.
5. Turkel'taub G.N., Chernyshev E.A. // Vestnik MITHT (Fine Chemical Technologies). 2008. V. 3. № 1. P. 46–49. (in Russ.).
6. Kharitonov N.P., Ostrovskij V.V. Termicheskaya i termookislitel'naya destrukciya (Thermal and thermooxidative destruction). Leningrad: Nauka Publ., 1982. 208 p. (in Russ.).
7. Turkel'taub G.N., Chernyshev E.A. // Sorbcionnye i khromatograficheskie processy (Sorption and chromatographic processes). 2005. V. 5. № 3. P. 305–312. (in Russ.).
8. Sobolevskij M.V., Skorokhodov I.I., Grinevich K.P. Oligoorganosiloksany (Oligoorganosiloxanes). M.: Khimiya, 1985. 264 p. (in Russ.).