

CHROMSYMP. 306

## HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF ORGANOMETALLIC COMPOUNDS

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### SUMMARY

High-performance liquid chromatography (HPLC) was applied to the separation and analysis of organometallic compounds (OMC) of the following classes: (1) sterically hindered silicon-containing phenols and some of their alkyl-substituted analogues; (2) silyl-, alkyl- and bromine-substituted naphthalenes; (3) tri- and pentaphenyl derivatives of phosphorus, antimony and bismuth; and (4) ferrocenyl and cymanthrenyl derivatives of antimony and bismuth. Optimal separation conditions were determined and the main retention regularities on Silochrom C-80 and Silasorb 600, when using *n*-hexane containing 0-3% (v/v) of diethyl ether as the eluent, are discussed. Examples of the separation and analysis of reaction and artificial mixtures of OMC with similar structures carried out by normal-phase HPLC are given.

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### INTRODUCTION

Many publications (see, in particular, two reviews<sup>1,2</sup>) have been devoted to the application of high-performance liquid chromatography (HPLC) to the separation and analysis of organometallic compounds (OMC). There are two principal reasons for this activity. On the one hand, many OMC with theoretical and practical importance are either thermally unstable (for example, silicon-containing phenols undergo thermal rearrangement into the corresponding phenoxysilanes<sup>3</sup>) or of low volatility (for instance, the molecular masses of the ferrocenyl and cymanthrenyl derivatives of bismuth described in this paper are 770 and 821, respectively). This rules out the possibility of the application of gas chromatography to the analysis of such OMC. On the other hand, liquid chromatography (LC) requires mild separation conditions; there is no need to convert sample compounds into the vapour phase and most separations can be carried out at room temperature. However, the most important aspects are that modern LC is characterized by high speed and efficiency.

We have used LC for the separation and analysis of OMC for approximately 10 years, during which many classes of thermally unstable and low-volatile OMC have been investigated<sup>4</sup>. However, at the beginning it was substantially a period of

instrumental development of classical LC with all its limitations (long analysis time, low efficiency of the separation, etc.). In this paper the possible application of normal-phase HPLC to the separation and analysis of some new OMC is considered.

## EXPERIMENTAL

All the investigations were carried out on a Tsvet-304 liquid chromatograph equipped with a UV detector (254 nm) and stainless-steel columns (190 × 4 mm I.D.). Silasorb 600 (*ca.* 5  $\mu\text{m}$ ) (Lachema, Brno, Czechoslovakia) and home-made Silochrom C-80 (*ca.* 6  $\mu\text{m}$ ) with specific surface areas of 600 and 80  $\text{m}^2/\text{g}$ , respectively, were used as adsorbents. The columns were packed using the slurry-packing method<sup>5</sup>. The column efficiency was up to 79,000 theoretical plates per metre (with respect to nitrobenzene). *n*-Hexane containing 0–3% (v/v) of diethyl ether was used as the eluent at a flow-rate of 1–2  $\text{cm}^3/\text{min}$ . The input pressure was 40 atm (*ca.* 4 MPa). All the measurements were made at room temperature (22°C). The samples (1  $\mu\text{l}$ ) were dilute solutions of the investigated compounds in *n*-hexane and were injected with a 10- $\mu\text{l}$  syringe. Both artificial and reaction mixtures of OMC were used for the separation.

## RESULTS AND DISCUSSION

### *Sterically hindered silicon-containing phenols*

Many papers have been devoted to the analysis of phenols by HPLC (see, for example, a review<sup>6</sup>). However, as far as we know, sterically hindered silicon-containing phenols have been mentioned only in one paper<sup>4</sup>, which reflects the period when the columns of low efficiency were used, which permitted only a group separation of phenols. The influence of a variation in *ortho*- and *para*-substituents (in particular, the replacement of a silyl group with a corresponding alkyl group) was not observed. HPLC makes it possible to separate tri-substituted phenols and to establish the influence of *ortho*- and *para*-substituents.

Table I gives the retention times ( $t_R$ ) determined experimentally for 27 sterically hindered silicon-containing phenols on Silasorb 600 when using *n*-hexane as the eluent. For the sake of convenience the investigated compounds are divided into 12 series (I, II, V, VII, XI, XII) and pairs (III, IV, VI, VIII, IX, X) in accordance with the type, number and position of substituents.

Table II shows, for comparison purposes, the retention times of some alkyl-substituted analogues of silicon-containing, phenols marked with asterisks in Table I.

*Influence of ortho-substituents on the retention of silicon-containing phenols.* As can be seen from Table I, the extent of the steric hindrance of the phenol hydroxy group with *ortho*-substituents plays the main role in the retention of the silicon-containing phenols investigated. Thus, the retention times increase when the hindrance of the phenol hydroxy group decreases [going from compounds of series I to those of pair II, and further to those of series V; going from compounds of series II to those of pair IV, and further to those of pair VI; the same happens when we go from the compounds of series (pairs) X, XI and VII to those of series V or from the compound 24 to compound 27 in series XII].

For compounds 1, 2 and 3 of series I (the 2-substituents are  $\text{SiEt}_3$ ,  $\text{SiEtMe}_2$

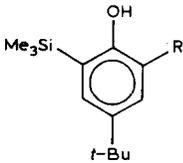
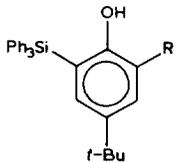
TABLE I

RETENTION TIMES ( $t_R$ ) OF STERICALLY HINDERED SILICON-CONTAINING PHENOLS ON SILA-SORB 600Me = CH<sub>3</sub>; Et = C<sub>2</sub>H<sub>5</sub>; *t*-Bu = C(CH<sub>3</sub>)<sub>3</sub>; *c*-Hex = cyclo-C<sub>6</sub>H<sub>11</sub>; Ph = C<sub>6</sub>H<sub>5</sub>.

Series (pair)	Compound No.	Compound	$t_R$ (min sec)	series (pair)	Compound No.	Compound	$t_R$ (min sec)
I				II			
	1	R = Et	2'21"		4	E = C	3'12"
	2	R <sub>3</sub> = EtMe <sub>2</sub>	2'46"		3*	E = Si	3'16"
	3*	R = Me	3'16"	5*	E = Ge	3'42"	
III				IV			
	6	R = Et	12'02"		8	E' = Ge, E'' = Si	6'43"
	7*	R = Me	42'	9	E' = Si, E'' = Ge	7'56"	
V				VI			
	10*	R = <i>t</i> -Bu	50'		14	R = H	49'
	11*	R = H	56'		15	R = Me	53'
	12	R = Me	58'				
	13	R = Br	87'				
VII				VIII			
	16*	R = <i>t</i> -Bu	3'00"		19	R = <i>t</i> -Bu	25'
	17	R = <i>c</i> -Hex	3'00"		20	R = <i>c</i> -Hex	28'
	18	R = Br					
IX				X**			
	21*	R = Me	3'35"		23*	R = SiMe <sub>3</sub>	2'55"
	22*	R = Br	3'38"	4	R = <i>t</i> -Bu	3'12"	

(Continued on p. 380)

TABLE I (continued)

Series (pair)	Compound No.	Compound	$t_R$ (min sec)	series (pair)	Compound No.	Compound	$t_R$ (min sec)
XI				XII			
	16*	R = Br	3'00"		24	R = SiEt <sub>3</sub>	4'45"
	3*	R = <i>t</i> -Bu	3'16"		8	R = GeMe <sub>3</sub>	6'43"
	9	R = GePh <sub>3</sub>	7'56"		19	R = Br	25'
	7*	R = Me	42'		25	R = SiPh <sub>3</sub>	50'
10	R = H	50'	26	R = Me	70'		
				27***	R = H	∞	

\* There are the corresponding alkyl-substituted phenols (not shown in Table I except compound 4, which is the *tert.*-butyl-substituted analogue of silyl-substituted phenols 3 and 23 and germlyl-substituted phenol 5).

\*\* Alkyl-substituted phenols with R = Ph, H, Br, Me, CPh<sub>3</sub>, NO<sub>2</sub>, O-*t*-Bu (mentioned in the sequence of increasing  $t_R$ ) were also investigated, but they are not discussed in this paper.

\*\*\* Not eluted in an acceptable time.

and SiMe<sub>3</sub>, respectively, where Me = methyl and Et = ethyl) with a large *tert.*-butyl (*t*-Bu) substituent in the 6-position, an increase in the dimensions of the 2-substituent and correspondingly of the extent of hindrance of the hydroxy group, results in a decrease in retention. The difference in the influence of a 2-substituent on the retention manifests itself more clearly in compounds 6 and 7 of pair III (the 2-substituents are SiEt<sub>3</sub> and SiMe<sub>3</sub>, respectively) with a less bulky methyl substituent in the 6-position in comparison with the corresponding *tert.*-butyl substituent in the compounds of series I.

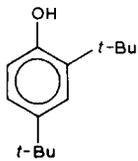
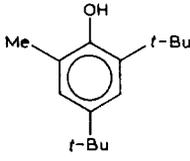
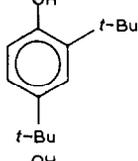
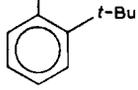
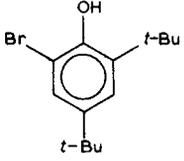
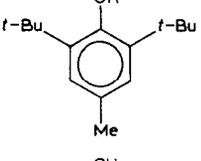
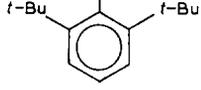
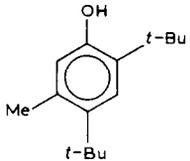
It is interesting to note how a variation in an element in the 2-substituent EMe<sub>3</sub> (E = C, Si, Ge) of compounds 4, 3 and 5 of series II influences the retention of phenols. Whereas for alkyl- and silyl-substituted derivatives the retention times differ slightly, the germlyl-substituted derivative is retained much more strongly (Fig. 1). It should also be noted that although compound 3 and its alkyl-substituted analogue 4 have very close retention times, alkyl-substituted analogues (see Table II) of the less sterically hindered *ortho*-silyl-substituted phenols 7, 10, 11, 16 and 22 (marked with asterisks in Table I) are eluted considerably faster than their silicon-containing analogues. As it has been established that the extent of the steric hindrance of the phenol hydroxy group has the greatest influence on the retention of phenols, chromatographic data make it possible to conclude that the hindrance of the phenol hydroxy group with a 2-substituent EMe<sub>3</sub> (E = C, Si, Ge) decreases in the order C > Si > Ge.

From this point of view, the stronger retention of compounds 19 and 20 of pair VIII in comparison with compounds 16 and 17 of series VII indicates less hindrance of the phenol hydroxy group with an SiPh<sub>3</sub> substituent than that with an SiMe<sub>3</sub> substituent in the 2-position.

One more example of the separation of silicon- and germanium-containing

TABLE II

RETENTION TIMES ( $t_R$ ) OF STERICALLY HINDERED ALKYL-SUBSTITUTED PHENOLS ON SILASORB 600

Compound No.	Compound	$t_R$ (min sec)	No. of silicon-containing analogue from Table I
1		3'12"	3, 5*
2		22'20"	7
3		26'35"	10
4		29'37"	11
5		2'15"	16
6		3'38"	21
7		3'32"	22
8**		90'	—

\* Compound 5 (see Table I) is a germanium-containing phenol.

\*\* Compound 8 from Table II is a positional isomer with respect to the compounds 2 and 6.

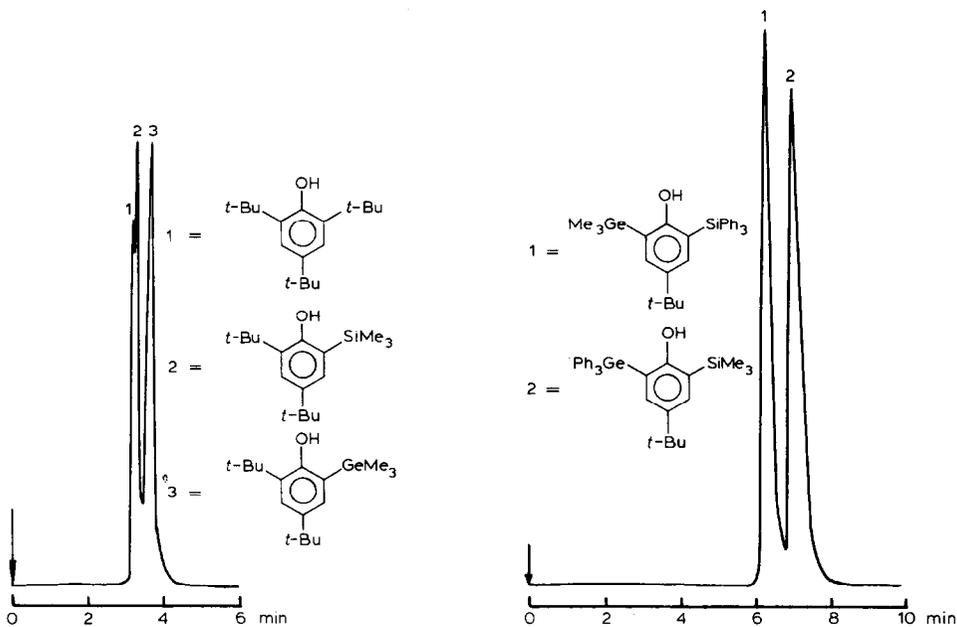


Fig. 1. Chromatogram of the separation of an artificial mixture of 2,4,6-tri-*tert.*-butylphenol (1), 2-trimethylsilyl-4,6-di-*tert.*-butylphenol (2) and 2-trimethylgermyl-4,6-di-*tert.*-butylphenol (3). Chromatograph, Tsvet-304 with a UV detector (254 nm) and a stainless-steel column (190 × 4 mm I.D.); adsorbent, Silasorb 600 (grain size *ca.* 5 μm); eluent, *n*-hexane; flow-rate, 1 cm<sup>3</sup>/min; temperature, 22°C.

Fig. 2. Chromatogram of the separation of an artificial mixture of 2-triphenylsilyl-4-*tert.*-butyl-6-trimethylgermylphenol (1) and 2-trimethylsilyl-4-*tert.*-butyl-6-triphenylgermylphenol (2). Conditions as in Fig. 1.

phenols is shown in Fig. 2. However, for compounds 8 and 9 of pair IV the simultaneous variation in the 2- and 6-substituents should be taken into account. In this instance it could be assumed on the basis of the retention times that the elution sequence of these compounds is caused by the resulting hindrance of the phenol hydroxy group.

A sharp decrease in the retention of silicon-containing phenols when bromine is introduced into the 6-position [going from compounds of series V to those of series VII or from compound 27 of series XII (which under the mentioned conditions is not eluted in an acceptable time) to compound 19 of pair VIII] is evidently explained by the presence of the Br ... HO- intramolecular hydrogen bonding, decreasing the ability for specific interaction of these compounds with the adsorbent.

The influence of a 2-substituent on the retention of the investigated silicon-containing phenols, when the 4- and 6-substituents are invariable, is greater in *ortho*-SiPh<sub>3</sub>-substituted phenols of series XII. The hindrance of the hydroxy group of these phenols decreases (and their retention correspondingly increases) for the series of 2-substituents in the order SiEt<sub>3</sub> > GeMe<sub>3</sub> > Br > SiPh<sub>3</sub> > Me > H. However, if one considers the similar series of SiMe<sub>3</sub>-containing phenols (series XI), the influence of a 2-substituent on the retention gives a different order of decrease of the hindrance of the hydroxy group: Br > *t*-Bu > GePh<sub>3</sub> > Me > H.

*Influence of para-substituents on the retention of silicon-containing phenols.* As the phenol hydroxy group plays the main role in the retention of the investigated silicon-containing phenols on Silasorb, as can be seen from Table I, the influence of *para*-substituents, non-adjacent to the hydroxy group, is as would be expected, weaker than that of the phenol hydroxy group hindering *ortho*-substituents. Nevertheless, various steric and electronic effects caused by different *para*-substituents and also a change in the adsorbate-eluent intermolecular interaction in most instances enable one to separate successfully by normal-phase HPLC silicon-containing phenols that differ only in the *para*-substituents.

It is known that alkyl substituents in the aromatic ring increase the electron density on the ring, and therefore phenols with a methyl substituent in the *para*-position (compounds 12 and 15) are retained more strongly than their analogues with a hydrogen in the *para*-position (compounds 11 and 14). However, silicon-containing phenols with a *tert.*-butyl substituent (compounds 10, 16, 6 and 19), in which a *tert.*-butyl substituent in the *para*-position also increases the electron density of an aromatic system, are always eluted faster than their analogues without a substituent in the *para*-position. In this instance the increase in the adsorbate-eluent intermolecular interaction plus a steric effect of a large *tert.*-butyl group prevail over the

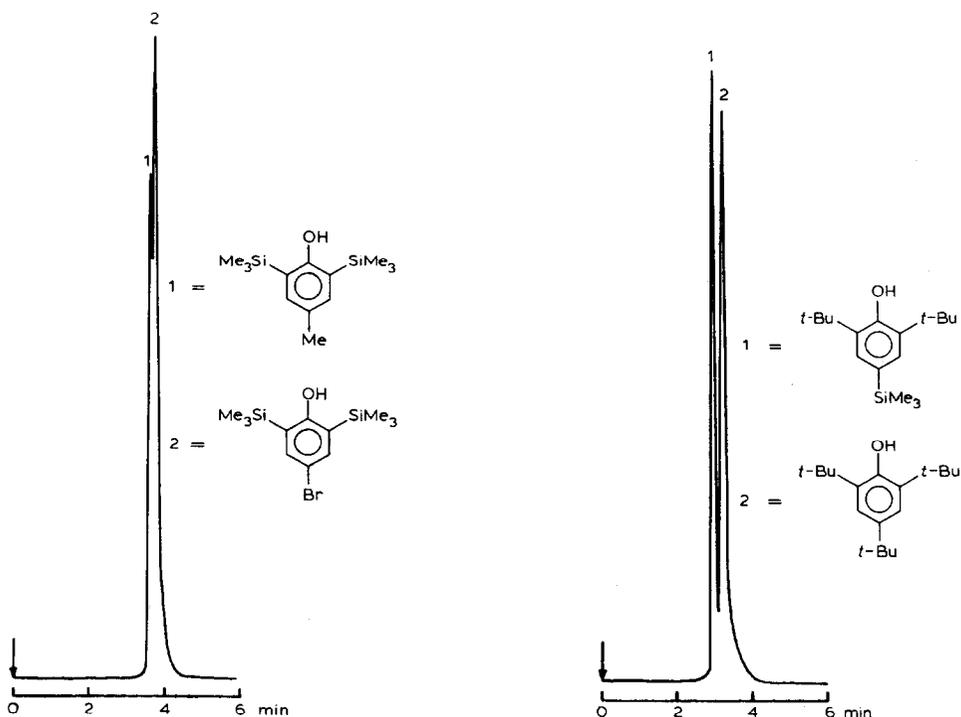


Fig. 3. Chromatogram of the separation of an artificial mixture of 2,6-di(trimethylsilyl)-4-methylphenol (1) and 2,6-di(trimethylsilyl)-4-bromophenol (2). Conditions as in Fig. 1.

Fig. 4. Chromatogram of the separation of an artificial mixture of 2,6-di-*tert.*-butyl-4-trimethylsilylphenol (1) and 2,4,6-tri-*tert.*-butylphenol (2). Conditions as in Fig. 1.

increase in the adsorbate-adsorbent intermolecular interaction due to the electron density increase on the ring.

The increase in retention of the silicon-containing phenols with a *tert.*-butyl substituent in the *para*-position (compounds 13, 18 and 22) in comparison with the corresponding compounds alkyl-substituted (compounds 10, 12, 16, 17 and 22) or unsubstituted (compounds 11 and 14) in the *para*-position is evidently explained only by electronic effects, as contributions to the adsorbate-eluent intermolecular interaction and steric effects for bromine and methyl groups are considered to be approximately equal.

In general, the influence of *para*-substituents on the retention of the investigated silicon-containing phenols is greater for a lower hindrance of the phenol hydroxy group (*e.g.*, the pairs of compounds 16, 17 and 19, 20, respectively). However, when the extent of the steric hindrance of the phenol hydroxy group increases it is possible, by means of a high-efficiency column, to carry out a satisfactory separation of phenols with various *para*-substituents, the retention times of which differ by only a few seconds (for example, compounds 21 and 22, pair IX; Fig. 3).

It should be noted that, whereas alkyl-substituted analogues (see Table II) are eluted before than the corresponding silyl-substituted phenols (marked with asterisks in Table I), compound 4 with a *tert.*-butyl substituent in the *para*-position is eluted later than the corresponding silyl-substituted phenol 23 (Fig. 4).

### *Substituted naphthalenes*

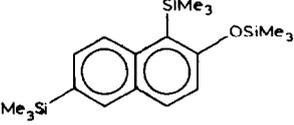
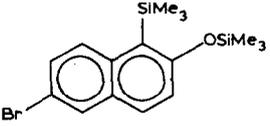
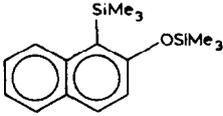
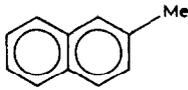
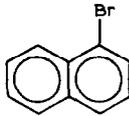
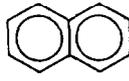
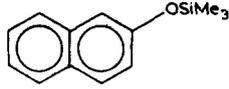
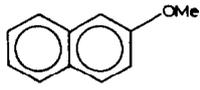
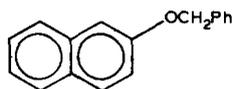
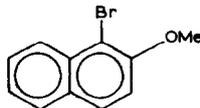
Numerous naphthalene derivatives including, for example, isomeric derivatives<sup>7</sup>, are successfully separated by HPLC. However, in this section we shall discuss the potential of the application of HPLC in combination with spectroscopic data to the investigation of substituted naphthalenes.

When the substituents in naphthalenes are replaced with others, a redistribution of the electron density takes place, which influences both the chromatographic and spectroscopic characteristics. Consequently, by examining these characteristics one can judge the variation of the electron density distribution.

Table III gives the retention times of fourteen substituted naphthalenes on Silasorb 600 with *n*-hexane as the eluent. The charge-transfer frequencies ( $\nu_{CT}$ ) in the electronic spectrum of a charge-transfer complex (CTC) of substituted naphthalenes with tetracyanethylene (TCE) are also given. Without going into detail (for which one may refer to ref. 8), it should be noted that the value of  $\nu_{CT}$  characterizes the distribution of the electron density in an aromatic system. There are elements with a formal analogy between the adsorption of substituted naphthalenes on Silasorb and the formation of CTC with TCE: in both instances substituted naphthalenes act as a donor (during the adsorption the protonated hydrogen atoms of the silanol hydroxy groups on the adsorbent surface act as an acceptor, and when CTC is formed TCE is an acceptor). It is obvious that, when large substituents are absent, the specific interaction of the  $\pi$ -electron system of naphthalene with the protonated hydrogen atoms of the silanol hydroxy groups on the adsorbent surface should make a dominant contribution to the retention of substituted naphthalenes on Silasorb 600. The greater the  $\pi$ -electron density of an aromatic system is, the greater the retention and the smaller  $\nu_{CT}$  should be.

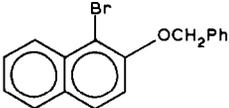
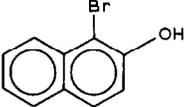
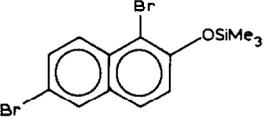
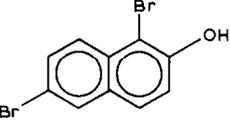
The relationship between the values of  $\log t'_R$  and  $\nu_{CT}$  for substituted naphthal-

TABLE III  
RETENTION TIMES ( $t_R$ ) OF SUBSTITUTED NAPHTHALENES ON SILASORB 600

Compound No.	Compound	$t_R$ (min sec)	$\nu_{CT}^*$ ( $cm^{-1}$ )
1		2'01"	—
2		2'12"	17,000
3		2'12"	16,500
4		2'21"	17,700
5		2'21"	18,400
6		2'21"	18,200
7		3'42"	16,900
8		7'06"	16,400
		7'42"	16,300
10		9'01"	16,700

(Continued on p. 386)

TABLE III (continued)

Compound No.	Compound	$t_R$ (min sec)	$\nu_{CT}^*$ ( $cm^{-1}$ )
11		9'44"	16,300
12		16'42"	16,950
13		18'45"	17,500
14		20'38"	17,600

\* The values of  $\nu_{CT}$  are taken from ref. 8.

enes is shown in Fig. 5. It is clear that there is a noticeable correlation (indicated by the dotted line) between the increase in the electron density in an aromatic system (decrease in  $\nu_{CT}$ ) and the increase in retention. The points corresponding to compounds 2 and 3 (the position and the type of substituents are indicated near the points) deviate from this correlation in the direction of smaller  $\log t'_R$  values because of (1) the decrease in the specific adsorbate-adsorbent intermolecular interaction due to the steric hindrances caused by large substituents in positions 1, 2 and 6; and (2) the increase in the non-specific adsorbate-eluent intermolecular interaction caused by the presence of these trimethylsilyl substituents. The points corresponding to compounds 12, 13 and 14 deviate from the correlation dependence in the direction of larger  $\log t'_R$  values because of (1) a stronger specific adsorbate-adsorbent intermolecular interaction due to the hydroxy groups (compounds 12 and 14) and an oxygen atom (compound 13); and (2) evidently a stronger non-specific adsorbate-adsorbent intermolecular interaction due to the contact of two or three substituents of small volume with the adsorbent surface.

Hence the comparison of chromatographic and spectroscopic data makes it possible to judge the variation of the electron density distribution in naphthalenes when one or another substituent is introduced.

#### *Tri- and pentaphenyl derivatives of phosphorus, antimony and bismuth*

We determined optimal conditions for the separation and analysis of the previously unexamined tri- and pentaphenyl derivatives of phosphorus, antimony and bismuth by HPLC. Table IV gives the retention times of some of these derivatives

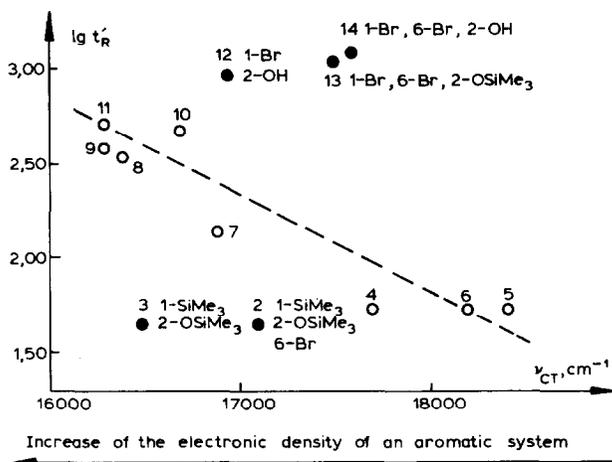


Fig. 5. Relationship between  $\log t'_R$  and  $\nu_{CT}$  for substituted naphthalenes. Points: compounds as in Table III.

on Silochrom C-80 and Silasorb 600 with both *n*-hexane and *n*-hexane containing 3% (v/v) of diethyl ether as the eluent.

The regularities of the retention of the investigated OMC are as follows.

(1) The retention times of the OMC, although they have the same elution order, are several times lower on Silochrom than on Silasorb. This is understandable, as these adsorbents have the same chemical nature of the surface, but differ in their specific surface areas (80 and 600 m<sup>2</sup>/g, respectively) and in their mean pore sizes (500 and 800 Å, respectively). Therefore, in our work, for the purpose of reducing the analysis time Silochrom is generally used for the separation of highly retained substances, for which elution from Silasorb was time consuming even with considerable additions of polar solvents to the non-polar eluent.

TABLE IV

RETENTION TIMES ( $t_R$ ) OF PHENYL DERIVATIVES OF PHOSPHORUS, ANTIMONY AND BISMUTH ON SILOCHROM C-80 AND SILASORB 600

No.	Compound*	$t_R$ (min sec)		
		Silochrom C-80 ( $\approx 6 \mu\text{m}$ ), 140 × 4 mm I.D.; <i>n</i> -C <sub>6</sub> H <sub>14</sub> + 3% (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	Silasorb 600 ( $\approx 5 \mu\text{m}$ ), 190 × 4 mm I.D.	
		<i>n</i> -C <sub>6</sub> H <sub>14</sub>	<i>n</i> -C <sub>6</sub> H <sub>14</sub> + 3% (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	
1	PhH	56"	1'46"	1'28"
2	Ph <sub>3</sub> P	1'13"	2'20"	2'16"
3	Ph <sub>3</sub> Sb	1'15"	3'03"	2'57"
4	Ph <sub>3</sub> Bi	1'17"	3'35"	3'13"
5	Ph <sub>3</sub> PO	2'21"	—	11'30"
6	Ph <sub>3</sub> P	1'06"	2'12"	1'50"
7	Ph <sub>3</sub> Sb	1'11"	2'55"	2'43"
8	Tol <sub>3</sub> Sb	1'02"	2'30"	2'06"

\* Ph = C<sub>6</sub>H<sub>5</sub>; Tol = *p*-C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>).

(2) In the series of the triphenyl derivatives of phosphorus, antimony and bismuth (compounds 2–5), there is an increase in retention on going from the phosphorus derivative to the bismuth derivative, and the presence of an oxygen atom in compound 5 results in an almost 5-fold increase in the retention in comparison with compound 2, which does not contain oxygen; it is evidently caused by the orientation of the oxygen atom in the direction to the adsorbent surface and by the strong specific interaction of the latter with the protonated hydrogen atoms of the adsorbent surface silanol hydroxy groups.

(3) Pentaphenyl derivatives of phosphorus and antimony (compounds 6 and 7, respectively) are retained more weakly than the corresponding triphenyl derivatives of these elements (compounds 2 and 3, respectively), as triphenyl derivatives have essentially a planar structure, whereas in pentaphenyl derivatives the three phenyl groups are arranged in one plane and the remaining two phenyl groups are perpendicular to it, which causes a different orientation in relation to the adsorbent surface and the possibility of intermolecular interactions with it. It is also possible that the retention of these compounds is affected by the fact that the non-specific interaction of phenyl groups with the eluent molecules in pentaphenyl derivatives is stronger than that for triphenyl derivatives. Obviously, the decrease in the retention of compound 8 in comparison with compound 7 is caused by a stronger non-specific inter-

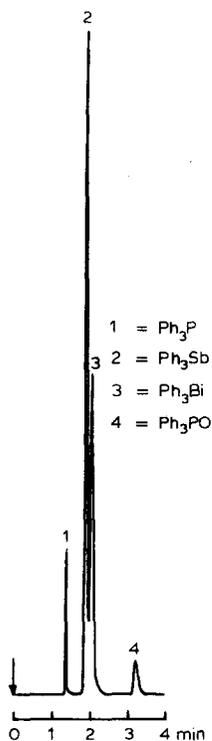
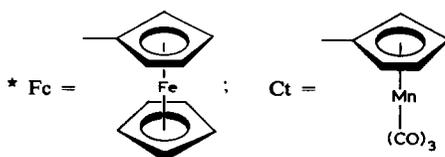


Fig. 6. Chromatogram of the separation of an artificial mixture of triphenyl derivatives of phosphorus, antimony and bismuth. Conditions as in Fig. 1, except the eluent was *n*-hexane + 3% (v/v) of diethyl ether at a flow-rate of 2 cm<sup>3</sup>/min).

TABLE V

RETENTION TIMES ( $t_R$ ) OF FERROCENYL AND CYMANTHRENYL DERIVATIVES OF ANTIMONY AND BISMUTH ON SILOCHROM C-80 AND SILASORB 600

No.	Compound*	$t_R$ (min sec)		
		Silochrom C-80 ( $\approx 6 \mu\text{m}$ ), 140 $\times$ 4 mm I.D.; $n\text{-C}_6\text{H}_{14}$ + 3% $(\text{C}_2\text{H}_5)_2\text{O}$	Silasorb 600 ( $\approx 5 \mu\text{m}$ ), 190 $\times$ 4 mm I.D.	
		$n\text{-C}_6\text{H}_{14}$	$n\text{-C}_6\text{H}_{14}$ + 3% $(\text{C}_2\text{H}_5)_2\text{O}$	
1	FcH	58"	2'21"	1'34"
2	Fc <sub>3</sub> Sb	1'06"	—	7'40"
3	Fc <sub>3</sub> Bi	1'00"	—	7'00"
4	CtH	1'16"	3'07"	2'05"
5	Ct <sub>3</sub> Sb	4'30"	—	18'00"
6	Ct <sub>3</sub> Bi	3'00"	—	14'40"
7	PhCt <sub>2</sub> Bi	1'30"	—	5'14"



action of the eluent with the toluyl fragments of the antimony organic derivative than with the phenyl fragments of OMC.

Fig. 6 shows the chromatogram for the separation of the artificial mixture of phosphorus, antimony and bismuth derivatives on Silasorb. A good separation of the OMCs was achieved in 4 min, which enabled these OMCs to be separated rapidly.

#### Ferrocenyl and cymanthrenyl derivatives of antimony and bismuth

Normal-phase HPLC was applied to the separation of previously unexamined ferrocenyl and cymanthrenyl derivatives of antimony and bismuth. Table V gives the retention times of these derivatives on Silochrom C-80 and Silasorb 600 with  $n$ -hexane containing 3% (v/v) of diethyl ether as the eluent.

The retention times of both ferrocenyl (compounds 2 and 3) and cymanthrenyl (compounds 5 and 6) derivatives decrease on going from the antimony to the bismuth derivatives, and the cymanthrenyl derivatives are retained approximately twice as strongly as the corresponding ferrocenyl derivatives. Apparently, this is associated with the presence of the carbonyl (CO) groups, and with an increase in the specific intermolecular adsorbate-adsorbent interaction and a decrease in the non-specific intermolecular adsorbate-eluent interaction for the cymanthrenyl antimony and bismuth derivatives in comparison with the ferrocenyl derivatives.

It is interesting that the replacement of one cymanthrenyl group by a phenyl group (going from compound 6 to 7) results in a sharp decrease in retention, as in this instance the intermolecular adsorbate-adsorbent interaction becomes weaker and the intermolecular adsorbate-eluent interaction becomes stronger.

In Fig. 7 shows the chromatogram and analysis conditions for phenyldicy-

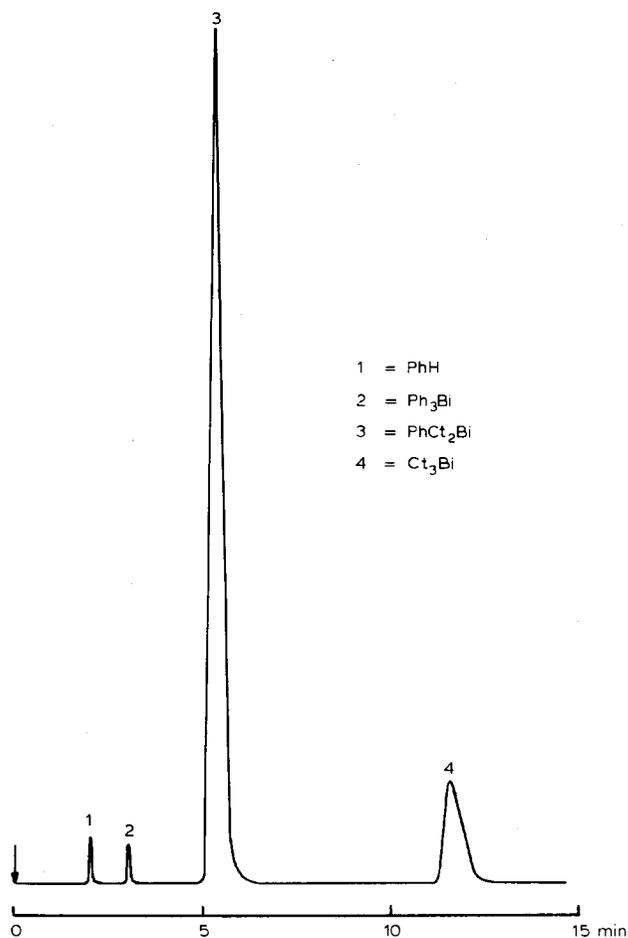


Fig. 7. Chromatogram of the qualitative determination of impurities in PhCt<sub>2</sub>Bi. Conditions as in Fig. 6, except the flow-rate was 1 cm<sup>3</sup>/min.

manthrenylbismuth (after a preliminary purification) on Silasorb. It can be seen that in the compound shown (peak 3) small amounts of the identified impurities are present. After the final purification they were removed, which was confirmed by the HPLC analysis.

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