

CHREV 189

SOVIET POLYSILOXANE STATIONARY PHASES FOR GAS CHROMATOGRAPHY

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1 INTRODUCTION

Polysiloxanes are currently the materials most commonly used as stationary phases in gas chromatography (GC). According to the data of Haken^{1,2}, extracted from literature sources, the proportion of polysiloxanes among all stationary phases increased from 40 to 60% between 1969 and 1977, and there has been a further increase since then³.

In the past lists of preferred stationary phases have been published, and in one report four out of the six listed are polysiloxanes⁴. These materials ideally meet the major requirements imposed on stationary phases, as they are chemically inert and cover almost the entire range of chromatographic polarity when appropriate substituents are introduced.

In the Soviet Union, a wide range of polysiloxane gums^{5,6} and fluids^{7,8} has been produced. Many of them have been recommended for use as stationary phases in gas chromatography, although in recent years, in keeping with the worldwide trend

TABLE I
PHYSICAL CHARACTERISTICS OF POLYSILOXANE STATIONARY PHASES

Stationary phase	Substituents	$M_{in}^* \cdot 10^{-3}$	MWD ⁶		
			$\bar{M}_w \cdot 10^{-3}$	$\bar{M}_n \cdot 10^{-3}$	\bar{M}_w/\bar{M}_n
PMS-100	Methyl	3.5-4.6	8.0	4.4	1.84
PMS-1000	Methyl	6.4-10			
PMS-1 · 10 ⁵	Methyl	34-38			
PMS-1 · 10 ⁶	Methyl	220			
SKTN	Methyl	7.5-7.5			
SKT	Methyl	600-900	870	360	2.42
SKTV	Methyl, 0.04% vinyl	600-900	600	240	2.50
SKTE type A	Methyl, 8% ethyl	7.5-7.5			
VKZh-94	Ethyl	0.8	0.92	0.88	1.05
PES-V-2	Ethyl		2.0	1.5	1.33
PES-S-1 (132-24)	Ethyl				
PES-S-2 (132-25)	Ethyl				
PES-5	Ethyl	1.6-1.75			
SKTFV-803	4% Phenyl, 0.15% vinyl	150-400	460	200	2.30
FM 1322/300 (133-158)	Low phenyl content	1.6-2.4			
FM-6	Low phenyl content	3.0			
SKTTs	Methyl, phenyl				
Lestosil	Methyl, phenyl				
SKTA-1	See text	400-2000			
DFOK	See text	200-1000			
Copolymer-2	< 50% Phenyl	0.7-0.8			
Copolymer 2/300	< 50% Phenyl	1.2-1.6			
Copolymer-3	< 50% Phenyl	2.7-3.2			
PFMS-2	50% Phenyl	0.6-0.7			
PFMS-4	50% Phenyl (35% eff.)	1.2-1.5	2.1	1.4	1.50
PFMS-5 (133-165)	Phenyl (48% eff.)	1.1-1.3	1.7	1.3	1.29
SKTF-100	50% Phenyl	140-680	190	110	1.78
PFMC-6 (133-57)	Phenyl (58% eff.)	1.3-1.6	1.0	0.9	1.11
KhS-2-1	Chlorophenyl	1.5-2.5	3.1	2.0	1.55
KhS-2-IVV (162-170VV)	Chlorophenyl	2.8			
SF	See text				
FS-169 (161-56)	Trifluoropropyl (11.5% eff.)	1.6			
FS-169/300 (161-89)	Trifluoropropyl (11.5% eff.)	3.2	3.4	2.8	1.21

d_4^{20}	Viscosity, cS, 20°	n_D^{20}	Cubic expansion coefficient, 10^3 deg^{-1} at 100°C	Vapor pressure, mm Hg		
				200°C	250°C	300°C
0.97	100 ± 10	1.405	0.96	2.2	7.9	22
0.98	1000 ± 100	1.406	0.95	0.3		1.0
0.98	$1 \cdot 10^5 \pm 1 \cdot 10^4$	1.406	0.95			
0.98	$1 \cdot 10^6$	1.406				
0.975	Gum	1.410				
0.975	Gum	1.410				
0.975	Gum	1.410				
0.975	Gum	1.415				
0.949	40-52	1.446				
	40-52	1.446		0.5	3.0	13.5
1 ± 0.05	210-315	1.446		17.4	36.3	66.1
1 ± 0.05	180-305	1.446		8.7	21.4	45.7
1 ± 0.02	200-500	1.448	0.73			
0.975	Gum	1.430				
1.05-1.06	60-90		0.90	15.6	21.5	27.9
< 0.957	50	1.428		$1.7 \cdot 10^{-2}$	$7 \cdot 10^{-2}$	0.2
	Gum					
	Gum					
1.09	Gum	1.525				
1.04 ± 0.01	35	1.496		18.0	34.0	57.4
1.07 ± 0.01	160-220					
1.07 ± 0.01	220-400		0.82	4.7	13.7	33.1
1.02	20-30	1.497		1.0	10.6	46.3
1.10	600-1000	1.540	0.72	1.0	4.1	12.5
> 1.12	1000	1.557	0.58	2.2	11.7	45.0
1.13	Gum	1.555				
1.15	45/150°C	1.585	0.61	$4.4 \cdot 10^{-1}$	2.5	10.0
1.03	40-47	1.430	0.84	$9.2 \cdot 10^{-2}$	$2.2 \cdot 10^{-1}$	4.5
1.03-1.04	70-85	1.442	0.90	$3.5 \cdot 10^{-3}$	$5.8 \cdot 10^{-2}$	$5.9 \cdot 10^{-1}$
1.085-1.107	45-60	1.391	0.94			
1.1	50-70	1.392- 1.398		$2.7 \cdot 10^{-1}$	$9.2 \cdot 10^{-1}$	2.5

(Continued on p. 4)

TABLE 1 (continued)

Stationary phase	Substituents	M_{in}^* 10^{-3}	MWD ⁶		
			\bar{M}_w 10^{-3}	\bar{M}_n 10^{-3}	\bar{M}_w/\bar{M}_n
SKTFT-25	12.5% trifluoropropyl	95-475			
FS-328 (161-48)	Trifluoropropyl (15.5% eff)	2-3			
SKTFT-50	25% trifluoropropyl	11-58			
SKTFT-50X	25% trifluoropropyl	115-575			
FS-16 (161-90)	Trifluoropropyl 1 (28% eff)	1			
SKTFT-75	37.5% trifluoropropyl	270-675			
SKTFT-100	50% trifluoropropyl	300-800**	300-900**	200-370**	1.82-3.25
NFS-100	50% trifluoropropyl	15-78			
FS-303 (161-126)	Trifluoropropyl (62% eff)	2.4-2.7	2.9	2.3	1.27
NPS-25	12.5% cyanoethyl	1.5			
NPS-50	25% cyanoethyl	1.2	2.3	1.4	1.58
NPS-100	50% cyanoethyl	1.3			
NSKT-25	12.5% cyanoethyl	83-830			
NSKT-33	16.5% cyanoethyl	87-870			
NSKT-50	25% cyanoethyl	93-930			
NSKT-100	50% cyanoethyl	113-1130			
γ -NSKT-100	50% cyanopropyl	127-1270			

* The values of M_{in} for fluids characterize \bar{M}_n and were taken from refs 7-10 and 19. The values of M_{in} for gums characterize \bar{M}_w and were calculated from the degree of polymerization (see refs 23 and 37).

** The MWD data for SKTF-100 were taken from ref 100.

to reduce the number of stationary phases, many Soviet chromatographers have used Western speciality polysiloxanes.

Soviet polysiloxanes used as stationary phases are reviewed here for several reasons. First, modern comprehensive reviews are not available and some conflicting and incomplete data have made it difficult to determine suitable alternatives. Soviet polysiloxanes have been briefly described in earlier Western reviews but are now presented here in greater detail. In this work the properties of frequently employed materials and some that are now virtually obsolete are included.

Second, to ensure that the wealth of data that have been published in the Soviet literature¹⁻³ could be used as fully as possible, the analogues produced in the West are indicated where available.

Third, as indicated in earlier reviews¹⁻³, some polysiloxane stationary phases developed in the Soviet Union have virtually unknown structures and are not available to chromatographers in other countries.

d_4^{20}	Viscosity, cS, 20°	n_D^{20}	Cubic expansion coefficient, 10^3 deg.^{-1} at 100°C	Vapor pressure, mm Hg		
				200°C	250°C	300°C
1.065	Gum	1.400				
1.1	65-120	1.390- 1.395	0.98	$2.6 \cdot 10^{-1}$	$8.2 \cdot 10^{-1}$	2.1
1.15	Gum	1.395				
1.15	Gum	1.395				
1.09	40	1.385	1.07	1.9	13.0	63.8
1.240	Gum	1.387				
1.329	Gum	1.383				
1.329	Gum	1.383				
1.330	1000-1500	1.3818	0.83	$6.6 \cdot 10^{-1}$	2.4	7.2
0.998	80	1.439				
1.05	350	1.439				
1.09	1340	1.4664				
	Gum					
	Gum					
	Gum					
	Gum					
	Gum					

Fourth, a new standardized (alphabetical) nomenclature has been recently adopted in the Soviet Union and is used together with the older numerical nomenclature. Both nomenclatures are given in Tables 1 and 2, with the older nomenclature in parentheses.

Fifth, another area of interest is the role of the solid support with regard to the properties of stationary phases. The wide use of exclusion chromatography as a means for determining the quality of stationary phases and the pattern of the changes they undergo in the course of analysis is also included.

The physical properties of Soviet polysiloxane stationary phases, critically selected from different sources, are listed in Table 1 and their chromatographic characteristics are given in Table 2. The latter table does not include obsolete materials.

In view of the steadily improving instrumentation and increasing sensitivity of detectors, the literature often contains stringent criteria for the evaluation of the quality of stationary phases. The upper temperature limits of the range in which stationary phases can be used are given in Table 2.

TABLE 2
CHROMATOGRAPHIC CHARACTERISTICS OF POLYSILOXANE STATIONARY PHASES

Stationary phase	Substituents	Upper temperature limit	McReynolds (Rohrschneider) constants							Relative polarity, P (%) [*]	Analogue	Ref.
			X	Y	Z	U	S	L				
PMS-100	Methyl	250	15	55	43	65	42	44	9	DC-200	44	
SKT	Methyl	300	17	57	46	67	45	47	6-8	SE-30	44	
SKTV	Methyl, 0.04% vinyl	300	18	57	45	65	45			SE-31	47	
SKTE type A	Methyl, 8% ethyl	250	16	56	44	66	43	46	6-8		44	
VKZh-94	Ethyl	150	7	14	18	21	26	6	5		44	
PES-S-1	Ethyl		10	14	17	22	24	7			44	
(132-24)												
SKTFV-803	4% Phenyl, 0.15% vinyl	300	29	73	62	97	68	65	10	SE-52, SE-54	44	
SKTIs	Methyl, phenyl		79	114	114		141	130			46	
Lestosil	Methyl, phenyl		73	124	122		189	140			46	
PFMS-4	50% phenyl (35% eff)	280	105	145	149	223	185	165	24	DC-710	44	
			106	148	150	222	184				47	
PFMS-5	48% eff phenyl	250	142	176	182	267	233	210	30		44	
(133-165)												
SKTF-100	50% phenyl	330	145	181	186	272	240	217	36		23	
			(1.57)	(1.96)	(2.05)	(3.13)	(2.17)				43	
PFMS-6	See text, 58% eff phenyl	300	164	192	198	288	262	236	33	Similar to OV-22	44	
(133-57)												
SKTA-1	See text	350	(0.82)	(1.29)	(1.16)	(1.32)	(1.68)		21		23	
DFOK	See text, 27% eff phenyl	400	86	130	134	181	154	143			44	
			(1.18)	(1.64)	(1.69)	(1.56)	(1.90)				23	
SAF	Siloxarophenanthrene	300	(0.81)	(1.51)	(1.94)	(2.73)	(2.38)		33		36	

KhS-2-1	Chlorophenyl	300	22	67	66	87	65	56	9-10	Versilube F-50	44
SF	See text	320	27	128	173	188	239				30
FS-169 (161-56)	Trifluoropropyl	250	46	104	149	189	118	112	17		44
SKTFT-25	12.5% trifluoropropyl	300	(0.42)	(1.01)	(1.42)	(2.46)	(1.27)		15		23
FS-328 (161-48)	Trifluoropropyl (15.5% eff.)	250	55	116	169	215	137	130	20		44
SKTFT-50	25% trifluoropropyl	300	47	160	212	268	230				30
			73	141	207	272	172	159	21		44
			74	145	212	173	158				46
			73	142	207	266	172				47
SKTFT-50X	25% trifluoropropyl	300	(0.82)	(1.49)	(2.47)	(3.50)	(2.00)				23
FS-16 (161-90)	Trifluoropropyl (28% eff.)	150	66	132	192	247	158	148			44
SKTFT-75	37.5% trifluoropropyl	300	(1.22)	(1.98)	(2.97)	(4.00)	(2.52)		26		23
SKTFT-100	50% trifluoropropyl	285	143	232	350	456	303	278	32	QF-1	44
			(1.59)	(2.46)	(3.47)	(4.50)	(3.00)				23
FS-303 (161-126)	Trifluoropropyl (62% eff.)	200	179	272	419	527	366	337	42		44
NSKT-25	12.5% cyanoethyl	250	122	261	237	345	241	211	37		44
			(1.05)	(2.44)	(1.57)	(2.11)	(1.98)				23
NSKT-33	16.5% cyanoethyl	250	135	275	251	363	259	225	42		44
NSKT-50	25% cyanoethyl	250	(1.91)	(3.52)	(3.29)	(5.00)	(3.12)		53	Similar to XE-60	23
NPC-50	25% cyanoethyl	200	164	320	287	426	302	268	37		44
NSKT-100	50% cyanoethyl	250	325	573	474	656	547	501	71		44
			(3.94)	(6.26)	(5.48)	(8.50)	(5.30)				23
γ -NSKT-100	50% cyanoethyl	250	276	461	405	584	473	421			44
NPS-100	50% cyanoethyl	180	297	502	451	644	512	448	62	Similar to XF-1150	44

* The values of P for siloxane gums were mostly taken from refs. 16 and 20 and those for fluids from ref. 14

2 DEVELOPMENT OF SOVIET POLYSILOXANE STATIONARY PHASES

The first reports concerning the use of Soviet polysiloxanes as stationary phases were published by Berezkin and co-workers^{11,12} and later by Turkeltaub *et al.*¹³. The first comparative study of the chromatographic characteristics of Soviet polysiloxanes was undertaken by Rudenko *et al.*¹⁴, who investigated the properties of the methylsiloxane gums SKT and SKTV-1, methyl phenyl polysiloxane fluids and the copolymer PFMS-2 and their residues and have showed that the gum SKTV-1 is comparable to E-301. In subsequent work, Rudenko and co-workers^{15,16} examined the chromatographic characteristics of eight gums containing methyl, phenyl, trifluoropropyl and nitrile substituents in comparison with the elastomers SE-30, SE-52 and XE-60. Also described for the first time were the trifluoropropyl derivatives SKTFV-803, SKTFT-50 and SKTFT-100.

In the preparation of polysiloxane stationary phases, it is necessary to remove low-molecular-weight impurities and catalyst residues, by reprecipitation in order to enhance their thermal stability. The reprecipitation was conducted by the dropwise addition of ethanol-water (85:15) to a 50% solution of the polymer in chloroform, ethyl acetate or acetone. The use of a smaller proportion of water resulted in stable emulsions. The precipitated polymer was washed twice with 85% ethanol and dried in a vacuum desiccator over P₂O₅ for seven days. The stationary phases were applied on to silanized Chromosorb P in an amount of 10%. Rudenko *et al.*^{15,16} determined the upper temperature limits and the relative polarity (*P*) according to Rohrschneider¹⁷ (for a blend of butanol-1, butanol-2, and *tert.*-butanol) and found that the Soviet siloxane gums are equivalent to their foreign analogues in terms of thermal stability and separating power.

Syavtsillo *et al.*¹⁸ also studied comparatively, prior to the work of Rudenko *et al.*^{15,16}, twelve polysiloxane fluids. The study involved two diethyl polysiloxanes, three dimethyl polysiloxanes, five methyl phenyl polysiloxanes, including PFMS-2, PFMS-4 and PFMS-6, and the fluorosiloxane fluids FS-16 and the FS-169. Some physical properties of these phases were determined, and a correlation was established between their selectivity and dielectric constants.

Considerable work was carried out on polysiloxane stationary phases by Luskina and Turkeltaub¹⁹, who examined the chromatographic properties of 16 polysiloxane fluids containing methyl, phenyl, trifluoropropyl and cyanoethyl substituents and determined their upper temperature limits, relative polarities (for benzene-cyclohexane), separation factors for C₂₉-C₃₀ *n*-alkanes and the number of theoretical plates. All sorbents with polysiloxanes were first conditioned at 200-400°C in a flow of nitrogen for 200-500 h

In the first Soviet review, Luskina and Turkeltaub²⁰ discussed the results of studies of the thermal stability of stationary phases for high-temperature gas chromatography, emphasizing the conditioning procedure and the methods for determining the upper temperature limit. It was indicated that the best way of determining this parameter is experimentation under conditions approximating the real operation of the chromatographic column, as opposed to thermogravimetric methods, which produce widely variant and even conflicting results. The factors responsible for chemical transformations of the stationary phase in the column (oxidation, decomposition, etc.) were discussed, together with procedures for eliminating them

Extensive research involving the chromatographic characteristics of polysiloxane gums, including the development of new grades of elastomeric stationary phases, was carried out by Yudina, Sakodinskii and co-workers²¹⁻³¹. Some of their work²¹⁻²³ involved detailed studies of the properties of most grades of Soviet siloxane gums used as high-temperature stationary phases, such as the dimethyl polysiloxane SKT, the methyl phenyl polysiloxanes KSTF-100, SKTA-1 and DFOK, fluorosiloxanes of the SKTFT type and nitrilesiloxanes of the NSKT type. As a result of these experiments, the structures, basic physical properties, relative polarities, Rohrschneider constants³² and upper temperature limits were specified for all these polymers²³. The properties of the materials examined were compared with those of stationary phases manufactured by Ohio Valley and Supelco in the U.S.A.

Vigdergauz *et al.* proposed the use of and determined linear analogues of Rohrschneider constants for the fluids PMS-100³³ and FS-16³⁴.

Anvaer and Sakodinskii³⁵ published a comprehensive list of stationary phases, which covered the chromatographic properties of more than 150 commonly used phases, including many Soviet polysiloxanes. A special chapter in Haken's reviews^{1,2}, deals with these materials and Sakodinskii's review³⁶ lists the Rohrschneider constants and upper temperature limits of the new high-temperature polysiloxane phases containing carborane and aromatic rings. The properties of some polysiloxane gums³⁷ and fluids³⁸ can be found in the catalogues published by Reakhim, the agency responsible for sales of chemical reagents in the Soviet Union. All these data, plus information on the physical and chromatographic properties of polysiloxane stationary phases, included in earlier reviews³⁹⁻⁴¹ and reference books^{42,43} are included in Tables 1 and 2. The *Gas Chromatography Handbook* written by Kocev and translated into Russian from Bulgarian was expanded by Berezkin and Urin, who edited the translation, to include information on the stationary phases produced in the Soviet Union⁴².

Rohrschneider's system, expressing the capacity of stationary phases to be involved in various types of intermolecular interactions, has been evaluated³² and was further elaborated by McReynolds⁴⁵ and has become universally adopted.

The McReynolds constants for 28 Soviet siloxane stationary phases of different structural types were determined for the first time by Itsikson *et al.*⁴⁴. Particular attention was paid to the selection of the solid support. The criterion of a support's suitability was coincidence of the retention indices of a standard substance on a column with squalane and the McReynolds data⁴⁵. The effect of the solid support on the retention indices in determining McReynolds constants is discussed later in this review.

The McReynolds constants for several phenyl- and fluoroalkyl substituted-siloxanes were determined by other workers^{30,46,47}. Stolyarov and Kartseva⁴⁷ compared the polarities of various stationary phases, including SE-30, SKT, SKTFT-50, PFMS-4, Dexsil 400 GC and Silbor-1, using both the Rohrschneider-McReynolds system and a method based on the thermodynamic characteristics of solution⁴⁸. Table 3 lists the differential molar free energies of solution ($-\Delta G$) calculated by the above workers in accordance with the latter method⁴⁸ for siloxane stationary phases. The McReynolds constants determined by Stolyarov and Kartseva⁴⁷ are included in Table 2. According to Stolyarov and Kartseva⁴⁷, the method for determining the polarity and selectivity of stationary phases, based on thermodynamic characteristics,

yields more information than the Rohrschneider–McReynolds system and permits a more reliable prediction of retention indices on various stationary phases.

As was shown in other work^{4,9}, the procedure commonly adopted for determining the content of polar substituents in polysiloxanes from the structure of the elementary link is applicable only to gums. With fluids, the actual content of the substituents is usually lower and depends on the molecular weight owing to the contribution of the terminal (usually methyl) groups.

Some polysiloxane stationary phases produced in the U.S.S.R. have been included in lists of materials recommended for use in gas chromatography. These lists have been compiled taking account of the relative polarities⁵⁰ and linear analogues of the Rohrschneider constants^{3,4} and McReynolds constants^{51,52}. Fridman and Vigerdgaуз^{50,53} evaluated the sorptive capacity of the liquids PMS-100, PMS-500, PFMS-4, NPS-50 and NPS-100 with respect to hydrocarbons, esters, ketones and alcohols. It has been shown that stationary phases of medium polarity (relative polarity $P = 30\text{--}60\%$), which are characterized by a high sorptive capacity with respect to any class of substance examined, are the most suitable for preparative chromatography.

Malakhov *et al.*⁵⁴ examined the suitability of the siloxanes PFMS-4, PMS-100, SKTFT-50 and SKTFV-803 for gas chromatography–mass spectrometry. Kanchenko *et al.*⁵⁵ reported values of the coefficients of cubic expansion of some polysiloxane fluids, necessary for determining the volume of stationary phase in the column at elevated temperatures. In view of the importance of this coefficient, we have included in Table 1 values taken from different sources^{7–10}. Studies of the thermal stability of polysiloxanes by thermal analysis have been reported in a number of papers. Thermogravimetry, differential thermogravimetry and differential thermal analysis have been used to determine the upper temperature limits of 36 stationary phases, including FS-16 and PFMS-4⁵⁶. The values obtained (120 and 250°C) are about 30°C below the commonly assessed values, probably because the materials had not been conditioned in advance. Further, as has been mentioned¹⁸, these methods often yield results that are at variance with chromatographic practice.

Luk'yanova *et al.*⁵⁷ and Rudenko *et al.*^{15,16} demonstrated, in thermogravimetric experiments, that the removal of catalyst residues from methyl phenyl polysiloxane fluids slows their decomposition at temperatures ranging from 350 to

TABLE 3

DETERMINATION OF THE POLARITY OF POLYSILOXANE STATIONARY PHASES FROM THE VALUE OF $-\Delta G$

Stationary phase	$-\Delta G_{CH_2}$ (cal/mole)	$-\Delta G_1$ (cal/mole)				
		Benzene	Butanol-1	Pentanone-2	Nitropropane	Pyridine
SE-30	452	2526	2432	2544	2757	2856
SKT	466	2482	2370	2487	2697	2822
SKTFT-50	439	2537	2563	3011	3380	3174
PFMS-4	492	2736	2632	2825	3303	3347
Dexsil-400	498	2743	2673	2888	3241	3266
Silbor-1	477	2704	4952	2918	3390	3583

400°C⁵⁵. A study of the chlorophenylsiloxane KhS-2-1 was described by Voznesenskaya *et al.*⁵⁸.

The thermal decomposition of polysiloxanes in an inert gas or vacuum has been studied by different workers⁵⁹⁻⁶⁶. Volchinskaya *et al.*⁵⁹ compared the thermal stabilities of methyl- and ethylsiloxane fluids in argon. Other groups have studied the thermal decomposition of dimethyl polysiloxanes^{60,61}, methyl phenyl polysiloxanes^{62,63}, methyl trifluoropropyl polysiloxanes⁶⁴, dimethyl (methyl dichlorophenyl) polysiloxanes⁶⁵ and phenyl metal polysiloxanes containing Mn, Co, Ni, Cu and Zn, in comparison with pure phenyl polysiloxane⁶⁶. The processes of thermal and thermo-oxidative decomposition of polysiloxanes were detailed by Kharitonov and Ostrovsky⁶⁷.

The common purpose of all of the above work was to define the areas of application of the materials under consideration. However, the results are also valuable in that they provide experimentally substantiated upper temperature limits, which are usually determined empirically. A knowledge of the thermal oxidative pattern of polysiloxanes permits the prediction of the service life of a chromatographic column as a function of its temperature and the oxygen content of the carrier gas. Some of the results reported in the above work have been used in analysing the properties of individual groups of polysiloxane stationary phases.

Itsikson and Moskaleva⁶⁸ used size exclusion chromatography to determine the molecular weight distribution (MWD) of about 30 siloxane stationary phases produced in the Soviet Union and elsewhere. Many materials were found to contain low-molecular-weight impurities, particularly the initial cyclic tetramers. Ainshtein *et al.*⁶⁹ described a GC technique for determining cyclic trimers and tetramers in methyl phenyl polysiloxane rubbers. Itsikson *et al.*⁷⁰ found that, during conditioning of the stationary phase in the column and also during its use near its temperature limits, the molecular weight of polysiloxane fluids increased with slight changes in their MWD and polarity. Andrianov *et al.*⁷¹ demonstrated the applicability of universal calibration according to Benoit *et al.*⁷² for the determination of the MWD of dimethyl polysiloxanes and methyl phenyl polysiloxanes by size exclusion chromatography.

A number of methods have been developed for determining various substituents in the polysiloxane chain by reaction or pyrolysis gas chromatography. These methods have been used to determine vinyl groups⁷³⁻⁷⁵, alkoxy groups⁷⁶, methyl groups of the $(\text{CH}_3)_3\text{-SiO}_{0.5-}$, $(\text{CH}_3)_2\text{-SiO-}$ and $\text{CH}_3\text{-SiO}_{0.5-}$ types⁷⁷, ethyl and phenyl groups⁷⁸, ethyl methyl, trifluoropropyl and diphenyloxy groups⁷⁹ and alkyl and phenyl group combinations^{80,81}. There are also reports on the analysis of the structural link ratio in methyl phenyl polysiloxanes⁸², the content of trifunctional links in dimethyl polysiloxanes⁸³ and the basic principles of the functional analysis of organosilicon compounds⁸⁴. The last subject has been reviewed by Luskina and Terent'yeva^{85,86}.

We have omitted work dealing exclusively with analytical applications using Soviet-produced siloxane stationary phases, as their application in the analysis of organosilicon compounds was treated in a definitive report by Shatz *et al.*⁸⁷ and a similar application in the analysis of terpenes was reported by Bardyshev *et al.*⁸⁸. Much information about the use of Soviet siloxanes for the analysis of unstable and reactive compounds can be found in a book by Ivanova and Frangulyan⁸⁹. The areas

of application of polysiloxane stationary phases are well known to specialists, and they can be clearly defined in terms of the phase structure and McReynolds or Rohrschneider constants. The examples given in this review are taken primarily from the first publications on a particular phase. The following sections deal with individual types of polysiloxane stationary phases.

3 ALKYL-SUBSTITUTED POLYSILOXANES

This group of stationary phases include siloxanes with methyl, vinyl and ethyl substituents. The most widely used dimethyl polysiloxane stationary phases in the Soviet Union include the gum SKT and the fluid PMS-100. In its structure and chromatographic characteristics, SKT is similar to the well known stationary phase SE-30. SKTN is a low-molecular-weight product with the same structure that has seldom been used as a stationary phase.

According to Rudenko *et al.*¹⁴, SKT gum has an inferior thermal stability to SKTV-1. We believe that their conclusion was the result of using a poor quality sample: comparison of the MWDs of the gums SKT, SKTV and SE-30⁶⁸ and experience with using this material suggest that all these gums are equivalent in terms of thermal stability and, after reprecipitation, SKT is virtually interchangeable with the specialty gum SE-30 GC.

The dimethyl vinyl polysiloxane gums SKTV (in ref. 16, this was misprinted as SKSV) and SKTV-1 contain 0.4 and 0.18% of vinyl group, respectively, and are close to the General Electric Company gum SE-31. The chromatographic characteristics of these materials are similar to those of the gums free of vinyl groups¹, which are frequently used in gas chromatography.

The PMS fluids are essentially dimethyl polysiloxanes with a linear structure, similar to DC-200, produced by Dow Corning (U.S.A.). The numerals following the name of the fluid indicate its viscosity, in centistokes, at 20°C. The PMS fluid range includes more than 40 grades with viscosities varying from 1 to $1.2 \cdot 10^6$ cS. Their properties have been described in detail elsewhere⁷. The fluid PMS-100 was first proposed for use in gas chromatography by Syavtsillo *et al.*¹⁸. Its upper temperature limit is 250°C but, after proper conditioning, this and many other polysiloxane fluids can be used at higher temperatures. For example, Turkeltaub and Luskina⁹⁰ analysed high-boiling organosilicon compounds on PMS-100 at temperatures of up to 340°C. The physical properties of some PMS fluids covering a broad range of molecular weights are listed in Table 2.

Fig. 1 shows chromatograms of some dimethyl polysiloxanes, obtained by an exclusion technique⁶⁸ on a Waters 200 instrument. These indicate that the MWD of SKTV gum is close to that of SE-30, but the former contains more high-molecular-weight fractions. In terms of MWD, SKT gum occupies an intermediate position between SE-30 and the higher molecular weight gum OV-1. The polydispersities of OV-1, SKT and SKTV are almost the same (2 and 2.5), whereas that of SE-30 is slightly lower (1.9). The PMS fluids exhibit a much lower molecular weight and a higher polydispersity (1.84) than OV-101 (1.35).

Polysiloxanes containing longer chain aliphatic substituents include the gum SKTE, grade A, containing 8% of diethyl siloxane links and 0.06% of vinyl groups, and the diethyl polysiloxane fluids BKZh-94 and PES-1-S. The low content of ethyl

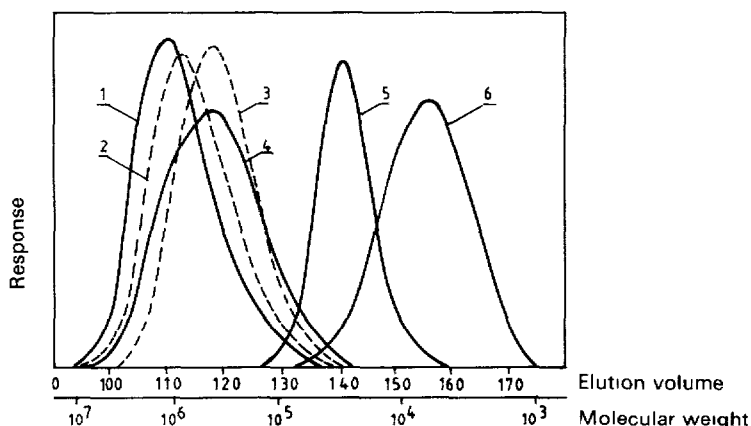


Fig 1 Size exclusion chromatograms of dimethyl polysiloxane stationary phases 1 = OV-1; 2 = SKT, 3 = SE-30; 4 = SKTV-1, 5 = OV-101; 6 = PMS-100

groups in SKTE gum (8%) does not significantly affect its polarity, and its use as a stationary phase offers virtually no advantages over SKT and SKTV. Complete replacement of methyl by ethyl groups in the polysiloxane molecule substantially reduces the polarity of the stationary phase

Determination of the McReynolds constants⁴⁴ has shown that the diethyl siloxanes BKZh-94 and PES-S-1 have almost the same polarity as the reference hydrocarbon ($C_{87}H_{176}$) developed by Kováts and hydrogenated Apiezon M (MH)⁹¹ and are less polar than dimethyl siloxanes and Apiezon L. The sums of the first five McReynolds constants for diethyl siloxane stationary phases, hydrocarbon $C_{87}H_{176}$, Apiezon MH, SE-30 and Apiezon L are 86–87, 71, 82, 217 and 143, respectively. The fluid BKZh-94 was first used by Turkeltaub *et al.*⁹² to separate a mixture of $SiCl_4$, $COCl_2$, HCl and Cl_2 and was widely employed in early work. The main drawback of this popular fluid is its low upper temperature limit of 140–150°C.

The maximum working temperature of a stationary phase is determined primarily by two parameters: thermal stability and vapour pressure at the limiting temperature.

Volchinskaya *et al.*⁵⁹ showed that the thermal stability of diethyl polysiloxanes is higher than that of dimethyl and dimethyl phenyl polysiloxanes. The decrease in viscosity at 100°C after exposure for 100 h in argon at 350°C was 12% for PMS-100, 17% for PFMS and only 5% for PES. When the temperature was increased to 375 and 400°C under the same conditions, the viscosities of the two ethyl-substituted polysiloxanes decreased by 18 and 20%, respectively.

The vapour pressure of polysiloxane fluids of the same structure decreases inversely with the molecular weight and directly with the content of low-volatility oligomers. Therefore, it would be appropriate at this juncture to consider the properties of some diethyl polysiloxane fluids produced in the U.S.S.R.⁶ and not used previously in gas chromatography. The highest molecular weights are exhibited by PES-5 and PES-S-1 and the lowest vapour pressure (10^{-6} – 10^{-8} mmHg at 20°C) by PES-V-2, which is an improved version of the fluid BKZh-94, free of low-molecular-weight oligomers. Comparison of its physical properties with those of the dimethyl-

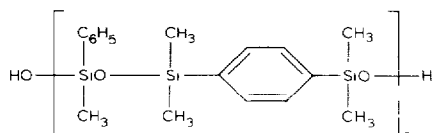
yl polysiloxane PMS-100 (upper temperature limit 250°C) indicates that the upper temperature limit of these fluids, after conditioning, will be at least 220–250°C. Hence these materials may be regarded as promising for use as “zero”-polarity stationary phases.

4 PHENYL-SUBSTITUTED POLYSILOXANES

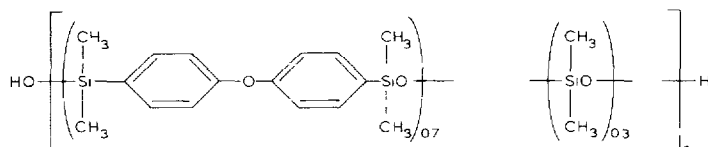
This group of stationary phases is available in the largest number of grades. Soviet industry produces a broad range of methyl phenyl polysiloxane fluids with linear, branched and cyclic structures⁹ and various grades of gums containing phenyl groups.

The gum SKTFV-803, first studied by Rudenko *et al.*¹⁴ and subsequently frequently used in chromatography, contains 4% phenyl substitution and 0.15% vinyl substitution, and is thus similar in composition to the gum SE-54. The gum SKTF-100 (50% phenyl substitution) is similar in structure to OV-17 but has a much higher molecular weight.

It has been reported that the introduction of phenylene groups into the main chain increases the thermal stability of polysiloxanes by 60–100°C⁴¹. Of particular interest are the stationary phases proposed for chromatography by Yudina *et al.*²⁶, namely the gums SKTA and DFOK, which contain propylene or diphenyl oxide groups in the main chain. The liquid phase SKTA-1 has the general formula

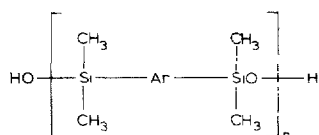


where $n = 1000\text{--}5000$ and DFOK has the formula



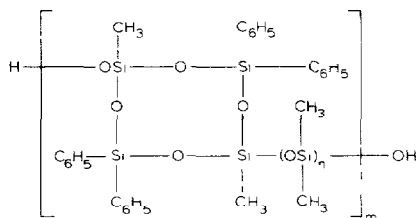
where $n = 1000\text{--}5000$.

The first reports on the use of DFOK were published by Yuzhelevsky *et al.*⁹³ (in the separation of stereoisomers of methylphenyl dimethyl cyclosiloxanes) and Yudina and Voronkina⁹⁴ (in the analysis of a repellent mixture). The application of SKTA gum in high-temperature preparative chromatography has been described²⁴. As regards polarity, SKTA-1 and DFOK occupy an intermediate position between OV-7 and OV-11 and are characterized by good selectivity and high upper temperature limits (350–400°C). Similar materials having the general formula



where Ar = C₆H₄ or C₆H₄OC₆H₄, were recommended by Sivtsova *et al.*⁹⁵, but they have not yet found much use.

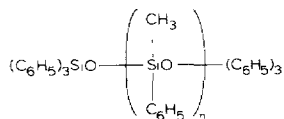
Also proposed as high-temperature stationary phases are polysiloxanes with siloxarophenanthrene groups in the side-chain²⁷, named SAF³⁶, and cycloliner siloxanes²⁸ of the general formula



where $n = 3-20$ and $m = 10-100$.

Prokopenko *et al.*⁴⁶ determined McReynolds constants for the phenyl-substituted gums SKTTs and Lestosil, but no data on their structure or thermal stability are available.

The chromatographic characteristics of methyl phenyl polysiloxane fluids have been studied by many workers^{20,44,50}. The most commonly used is the fluid PFMS-4^{11,12}, whose analogue is DC-710 and PFMS-6 with triphenyl terminal groups and the general formula



The fluid PFMS-4 was introduced into chromatography by Berezkin and co-workers^{11,12} and Turkeltaub *et al.*¹³. PFMS-6 and some other methyl phenyl polysiloxane fluids have been used by Turkeltaub *et al.*⁹⁶ for separating phenylchlorosilanes.

In earlier work, Itsikson and Snegirev⁴⁹ proposed the determination of the effective content of polar groups in phenyl- and trifluoropropyl-substituted polysiloxanes, thus permitting an objective comparison of the chromatographic polarities of various materials.

Table 4 lists comparative contents of phenyl substituents in some methyl phenyl polysiloxanes, the comparison being in terms of the elementary link structure and based on the method described earlier⁴⁹. It is evident that the effective contents of the phenyl substituents in the polysiloxanes OV-11, PFMS-4 and DC-710 are virtually the same. The McReynolds constants for these stationary phases also coincide.

Fig. 2 shows size exclusion chromatograms of four stationary phases with similar structures, containing 50% phenyl substituents in the elementary link. Comparison of the curves indicates that three of the materials (not SP-2250) contain a low-molecular-weight impurity identified as a cyclic tetramer^{49,68}. The molecular weight of the major component of PFMS-4 is lower than that of DC-710, but the

TABLE 4

CONTENT OF PHENYL SUBSTITUENTS IN METHYL PHENYL POLYSILOXANE STATIONARY PHASES

Phenyl substituent content	Stationary phase							
	OV-11	PFMS-4	DC-710	OV-17	PFMS-5	OV-22	PFMS-6	OV-25
As determined from the elementary link structure	35	50	50	50	—	65	68*	75
As determined from NMR data		39		42			66	63
Effective content according to ref 49	33.5	35	36	40	48	55	58	64

* Calculated from the general formula and molecular weight

latter contains much more of the tetramer. The molecular weights of these stationary phases determined by vapour phase osmometry are virtually identical (1500–1600). The effective content of phenyl groups in PFMS-6 is 58% (this is less than the true content as a result of the steric hindrances that occur during the interaction of the sorbates with the triphenylsilyl terminal groups⁴⁹). PFMS-6 is very similar to OV-22 in terms of polarity, although its chemical structure is entirely different. The fluid PFMS-5, whose effective content of phenyl substituents is 48%, occupies an intermediate position between OV-17 and OV-22.

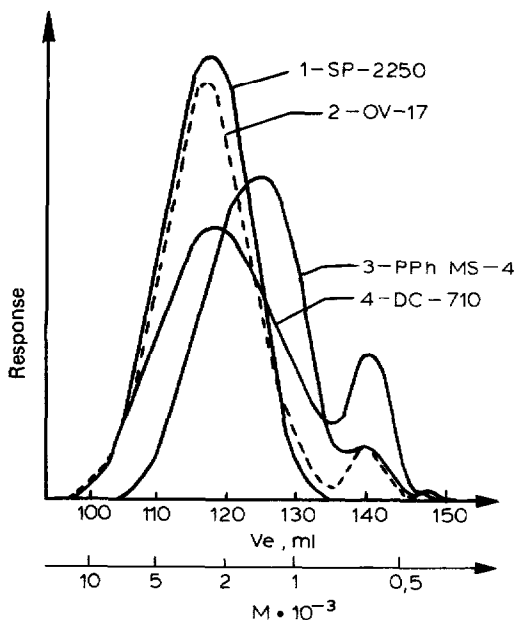


Fig. 2. Chromatograms of methyl phenyl polysiloxane fluids of similar structure: 1 = SP-2250; 2 = OV-17; 3 = PFMS-4; 4 = DC-710.

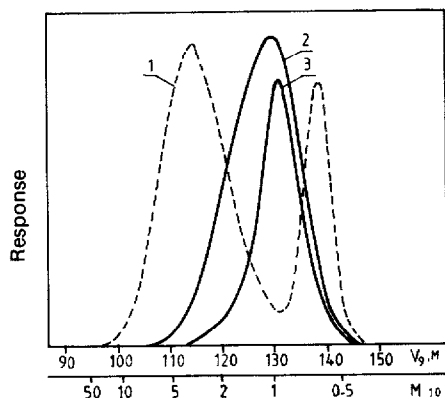


Fig 3 Chromatograms of methyl phenyl polysiloxane stationary phases with a high content of phenyl groups. 1 = OV-25, 2 = PFMS-5, 3 = PFMS-6

Fig. 3 shows for comparison size exclusion chromatograms of fluids with high phenyl substituent contents, *viz.*, PFMS-5, PFMS-6 and OV-25. The MWDs of the first two stationary phases are as expected, whereas OV-25 contains a considerable amount of low-molecular-weight substances, probably the starting cyclic compounds. The molecular weight of OV-25, determined by vapour phase osmometry, is 2100, that is, it approaches the value calculated from the chromatogram (1700 after calibration using polystyrene standards) but is much lower than the reported value¹ (10000). An investigation of two different OV-25 samples yielded similar results.

The upper temperature limit of commercial polysiloxane fluids is lower, in general, than that of gums, but after thorough conditioning they are capable of withstanding high temperatures¹⁸. For instance, the PFMS-6 fluids have been used for separating oligomers in methyl phenyl polysiloxanes at 320–400°C⁹⁷.

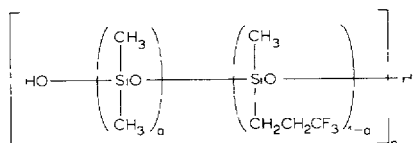
5. HALOGEN-SUBSTITUTED POLYSILOXANES

This group of stationary phases includes chlorophenyl- and trifluoropropyl-substituted polysiloxanes.

Chlorophenyl-substituted siloxane stationary phases have often been used in gas chromatography in recent years. Of the chlorophenyl siloxanes produced in the USSR¹⁰, the most suitable for use as stationary phases are the fluid KhS-2-1 and a similar fluid KhS-2-1VV that contains a smaller amount of lower molecular weight oligomers. The siloxane KhS-1 described in an earlier paper⁹⁸ is a modification of KhS-2-1.

The McReynolds constants for KhS-2-1 are higher than those for Versilube F-50 but lower than those for DC-560 and SP-400⁴⁴. As shown by Haken^{1,2}, chlorophenyl-substituted fluids of the DC-560 type have very similar polarities to the gum SE-52, which contains 5% phenyl substituents. The fluid KhS-2-1 is almost identical with another material containing the same proportion of phenyl substituents, DC-510, and their McReynolds constants are an average of 7–8 units below those of SE-52. However, the vapor pressure of KhS-2-1 is much lower, and its upper temperature limit is about 300°C.

The range of fluorine-containing siloxane stationary phases produced in the Soviet Union is extremely wide. The chromatographic properties of fluorine-containing gums have been studied in detail by Yudina and co-workers^{21-23,30,99} and Rudenko *et al.*¹⁶ and those of fluorine-containing fluids have been investigated by Luskina and Turkeltaub¹⁹ and Itsikson and co-workers^{44,49}. Gums of the SKTFT type are linear polymers with the general formula

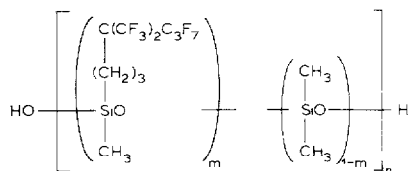


The numeral following the grade of the gum indicates the percentage of methyl trifluoropropyl siloxane groups. In high-molecular-weight polymers $n = 1000-5000$ and in low-molecular-weight polymers (SKTFT-50 and NFS-100) it is one order of magnitude lower. The gum SKTNFT-50 studied in early work^{16,44,49} seems to have an even lower molecular weight.

The fluorosiloxane gum SKTFT-100 is similar in polarity to the established materials QF-1 and OV-210 but, according to one report³⁰, it has a slightly higher upper temperature limit (285°C). The determination of the MWDs of different samples of this gum by turbidimetric titration has been described¹⁰⁰ and the results are summarized in Table 1. The other SKTFT gums with a lower content of trifluoropropyl substituents are even more thermally stable and have no analogues in the West²³. The upper temperature limit of these stationary phases is 300°C³⁰. A study in air at 250-430°C of the thermal stability of SKTFT gums containing 5, 33 and 100% of methyl trifluoropropyl siloxane links showed that substitution of trifluoropropyl groups for methyl ones at 290°C and above decreases the thermal stability of the polymer⁶⁴.

The most popular fluorosiloxane gum in the USSR is SKTFT-50, which was first used by Yudina *et al.*¹⁰¹ to separate cyclosiloxanes. This material gives good results in capillary columns with an efficiency of 1500 theoretical plates per metre with respect to chrysene) and in the preparative chromatography of high-boiling compounds^{24,103}. The separation of poorly chromatographed substances, such as alkyl- and oxygen-containing compounds of germanium, silicon and tin¹⁰⁴ and niobium and tantalum chlorides¹⁰⁵, has also been reported.

In 1980, Yudina *et al.*²⁹ proposed a high-temperature fluorine-containing stationary phase, SF, of general formula



where $m = 0.33-1$ and $n = 20-3000$. The properties of SF have been described elsewhere³⁰. Its upper temperature limit is 320°C. The McReynolds constants for SKTFT-50 and SF have been determined on columns containing 5% of stationary

phase on a non-silanized support³⁰ The constants determined for SKTFT-50 differ from those reported by other workers^{44,46,47}, which were similar to each other. The discrepancies are probably due to the effect of the type of support and the low content of the stationary phase on the solid support.

The physical properties of the fluorosiloxane fluids produced in the Soviet Union have been described elsewhere¹⁰. In earlier work, primarily FS-16 and FS-169 were used in preference to other stationary phases of this type. They were first proposed for gas chromatography by Syavtsillo *et al.*¹⁸.

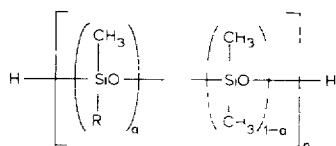
Studies of the chromatographic characteristics of some fluorosiloxane fluids have shown that most of them have similar polarities and, in some instances, thermal stabilities^{21,44} and have no analogues. As the chemical structures of these materials are not known, it is most appropriate to compare them in terms of the effective content of trifluoropropyl groups⁴⁹, shown in Table 1.

The fluid FS-16 (28% effective $\text{CH}_2\text{CH}_2\text{CF}_3$ groups) has a very similar polarity to the gum SKTFT-50, but exhibits a much lower upper temperature limit, and its use at present is restricted. Interesting properties are displayed by the fluid FS-303, proposed for use by Ainshtein *et al.*¹⁰⁰. The effective content of trifluoropropyl substituents in FS-303 is much higher than that in QF-1 (62 and 50%, respectively), and the McReynolds constant differences $Z-X$ and $Z-Y$ exceed those of QF-1 and OV-210 by 25–30 units. In some instances this may be important, particularly in the separation of mixtures containing alcohols or carbonyl compounds. The upper temperature limit of this stationary phase is 200°C.

As regards other fluorosiloxane fluids, the most commonly used is FS-169, containing 11.5% effective trifluoropropyl substituents and exhibiting a sufficiently high thermal stability. A similar fluid, FS-169/300, does not contain lower molecular weight oligomers.

6 CYANOALKYL-SUBSTITUTED POLYSILOXANES

The NSKT-type gums produced in the Soviet Union have the general formula

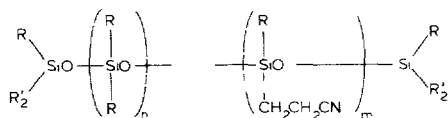


where $n = 1000-10000$ and $\text{R} = \beta$ -cyanoethyl (β -NSKT) or γ -cyanopropyl (γ -NSKT) In the former instance, the symbol of the substituent type (" β ") is often omitted. The numeral following the grade represents the percentage of the nitrile-containing group in the polymer molecule. NSKT gums were first proposed for use by Yudina *et al.*²⁵, who used them later as stationary phases¹⁰⁷. The gum NSKT-50 contains 25% of cyanoethyl groups and is similar to the widely used material XE-60. The other gums have no analogues.

The fluids NPS-25, NPS-50 and NPS-100 have the same general formula as the NSKT gums but differ from them by having trimethyl silyl terminal groups and a lower molecular weight. The chromatographic characteristics of these fluids were first described by Luskina and Turkeltaub²⁰, and those of the gums by other work-

ers^{16,21,23}. The McReynolds constants for some cyanoalkyl substituted siloxanes were determined in early work⁴⁴ and the MWD was studied later⁶⁸.

In terms of structure, the NPS fluids are similar to those of the XF type produced by General Electric (U.S.A.). However, their McReynolds constants (especially those of NPS-50) are lower than those of the XF type, probably owing to their lower molecular weights. Also proposed for use as stationary phases are fluids of the NPS type containing aryl substituents in the terminal groups¹⁰⁸. Their general formula is



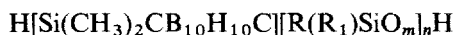
where R is C₁–C₁₀ alkyl, R' is aryl, $n = 0-15$ and $m = 5-30$.

The thermal stability of the above cyanoalkyl-substituted polysiloxanes is inferior to that of other types of siloxane stationary phases and does not exceed 230–250°C. Of these materials, those most commonly used in chromatography are the fluids NPS-50 and NPS-100 and the gum NSKT-50

7 CARBORANE-SILOXANE STATIONARY PHASES

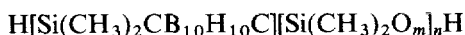
Carborane-siloxanes are an important class of stationary phases, their characteristic feature being high thermal stability.

In the early 1970s, linear *m*-carborane polysiloxanes¹⁰⁹ of the following type were first proposed as stationary phases in gas chromatography:



where R is C₁–C₈ alkyl, R₁ is C₆–C₁₀ aryl, $m = 1-5$ and $n \leq 50$. The commercially available compounds of this type, Dexsil-300, -400, and -410, have been widely and successfully used in chromatographic practice¹¹⁰. Carborane-siloxane stationary phases have also been used in the Soviet Union

Yudina *et al.*³¹ developed a carborane-siloxane stationary phase for the GC separation of organosilicon and organic compounds. This phase is essentially a high-molecular-weight siloxane polymer with carborane groups in the main chain and has the general formula



where $m = 1$ (KBS-1), 2 (KBS-2) or 3 (KBS-3), $n = 1000$ and the molecular weight is 10^5-10^6 . When $m = 2$ the stationary phase has the form of white crystals and when $m = 3$ it is a colourless rubber-like polymer. The upper temperature limit exceeds 500°C. It is recommended that KBS-2 and KBS-3 are coated on to a solid support in an amount of 20% (w/w) of the support (Chromaton N-AW). Yudina *et al.*³¹ gave examples illustrating the use of this phase for the chromatographic determination of methyl(propyl) dimethyl cyclosiloxanes, C₁₂–C₂₄ aromatic amines, polyphenyl esters, hexaphenyl cyclotrisiloxane and traces substances in aniline. When

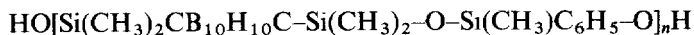
TABLE 5¹¹⁰

RETENTION CHARACTERISTICS OF METHYL ESTERS OF AROMATIC ACIDS ON DIFFERENT STATIONARY PHASES

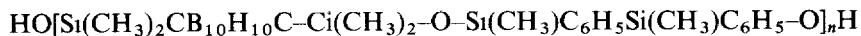
Chromatographed compound	Phenetidyl terephthalate		OV-17		XE-60		KBSN-3F		Polybutylene glycol succinate		PEG-40M	
	°C	I	°C	I	°C	I	°C	I	°C	I	°C	I
Methyl <i>n</i> -toluate			150	380	160	331	160	408	160	339	160	360
Methyl <i>m</i> -toluate			150	367	—	—	—	—	160	328	160	349
Dimethyl terephthalate	205	966	200	724	200	731	160	677	200	842	200	813
Dimethyl isophthalate	205	888	200	745	200	761	160	697	200	871	200	836
Methyl 2-naphthoate	265	1148	205	912	200	915	200	883	200	1044	200	1034
Trimethyl trimellate	205	1318	205	1121	200	1271	200	1034	210	1450	220	1380
Dimethyl 2,6-naphthalene dicarboxylate	205	1876	205	1377	200	1440	220	1272	210	1708	220	1654

used for the determination of trace impurities in aniline, KBS-2 gave better results than Dexsil-type stationary phases.

Later, Yudina *et al.*¹¹¹ proposed another type of carborane-siloxane stationary phase whose composition is given by the formulae



and

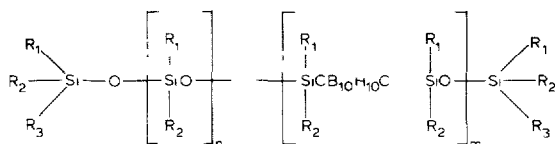


where $n = 10^3$ and the molecular weight is 10^5 – 10^6 . The first of the above two phases is usually referred to as KBS-2F and the other as KBS-3F. The upper temperature limit is above 450°C. The examples given¹¹¹ was the separation of mixtures of isopropylidiphenyl isomers

Chernyshev and Vigdergauz¹¹² studied the pattern of the chromatographic retentions of methyl esters of aromatic acids on various stationary phases, including silicones of the carborane type and their results are presented in Table 5. It can be seen that carborane-siloxanes of the KBS type are of low polarity. The Soviet carborane-polysiloxane phases of the KBS type for gas chromatography differ from the Dexsil-type phases in their much higher molecular weights. This is why the characteristics of these phases are more significantly affected by the main rather than the terminal groups of carborane-polysiloxanes. The Rohrschneider constants for some carborane-siloxane phases are listed in Table 6^{34,107–110}.

According to Anvaer and Sakodynskii³⁵, the Soviet high-temperature stationary phases KBS-1 and KBS-2 have similar properties to the Dexsil type. The properties of these phases are also discussed elsewhere^{36,109–113}.

To separate high-boiling organic compounds, Luskina *et al.*¹¹⁴ also proposed a carborane-siloxane stationary phase with the following structure:



where R_1 , R_2 and R_3 are alkyl-substituted or -unsubstituted aryls, $n = 3-24$ and $m = 1-8$. As shown by Luskina *et al.*¹¹⁵, materials of this type, containing terminal trimethylsiloxy, methyl-diphenylsiloxy and γ -trifluoropropylsiloxy groups, can be used as stationary phases in a wide temperature range of from -30 to 400°C and, for a short period of time, up to $450-500^\circ\text{C}$. The use of such carborane-siloxane stationary phases for the separation of high-boiling organosilicon compounds has been described^{116,117}

Recently, a new carborane-siloxane stationary phase, Silbor-1, was reported¹¹⁸. This is a viscous, rubber-like fluid readily soluble in toluene, benzene, methylene chloride and acetone and almost insensitive to oxygen. The working temperature range is $20-250^\circ\text{C}$, but special heat treatment has made it possible to expand this range to up to 350°C . The chromatographic characteristics of Silbor-1 in comparison with some other stationary phases are listed in Tables 7 and 8^{1,45,118}. It is evident from these tables that the most salient feature of Silbor-1 is its extremely high selectivity towards compounds containing a hydroxy group.

Comparison of all McReynolds constants, except Y , indicates that Silbor-1 is similar to Dexsil-410 in terms of polarity. However, as regards the relationship between Y and the other constants, this stationary phase should be classified as having extremely high selectivity⁵².

Silbor-1 has been used successfully to separate various perfume oils¹¹⁹ and to determine aldehydes in higher fatty alcohols and acids¹²⁰. Some of its characteristics have been reported by Loktev and Eliner¹²¹

TABLE 6

CHARACTERISTICS OF SOME SOVIET CARBORANE-SILOXANE STATIONARY PHASES

Name	Chemical type of phase, functional groups	Solvent	Upper temperature limit ($^\circ\text{C}$)	Rohrschneider constants				
				X	Y	Z	U	S
KBS-2	Carborane-siloxane, methyl	<i>n</i> -Hexane	500	0.55	0.79	1.14	1.61	1.08
KBS-3	Carborane-siloxane, methyl	Benzene	500	0.31	0.79	0.98	1.46	0.93
KBS-2F	Carborane-siloxane, methyl, phenyl	<i>n</i> -Hexane	450	0.80	1.54	1.53	2.19	1.58
KBS-3F	Carborane-siloxane, methyl, diphenyl	Benzene	450	0.61	1.40	1.37	2.06	1.48
Dexsil-300	Carborane-siloxane, methyl	—	450	0.42	0.84	1.16	1.56	1.27

TABLE 7¹¹⁸

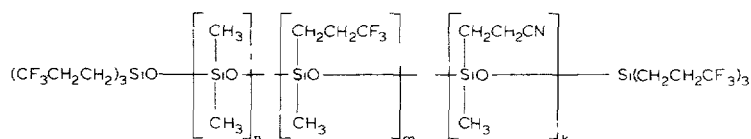
CHROMATOGRAPHIC CHARACTERISTICS OF VARIOUS STATIONARY PHASES

Stationary phase	Working temperature range (°C)	McReynolds constants				
		X	Y	Z	U	S
Dexsil-300 GC	40-450	42	84	116	156	127
Dexsil-400 GC	30-375	59	114	140	187	173
Dexsil-410 GC	20-360	85	165	169	242	180
Silbor-1	20-350	111	688	175	234	224
Quadrol	0-150	214	571	357	472	489
Hyprose SP-80	0-175	336	742	492	639	727

8 OTHER SILOXANE STATIONARY PHASES

This section deals briefly with some new siloxanes that differ in structure from those types already described, and also some copolymer materials.

Luskina *et al.*¹²² proposed mixed siloxanes containing methyl, β -cyanoethyl and trifluoropropyl groups and having the general formula



where $m = 0-20$, $n = 0-20$ and $k = 1-20$. These stationary phases have been found to be highly selective for the separation of fluorinated and perfluorinated compounds. The maximum column temperature is 235°C.

The new high-temperature material proposed by Luskina *et al.*¹²³ is essentially a dimethyl polysiloxane containing 2-25% of β -ethyladamantyl groups. Examples reported included the separation of a mixture of siloxanephenanthrene derivatives at temperatures programmed to rise to 350°C and the separation of pentaphenyl ether derivatives at 325°C

TABLE 8¹¹⁸

RETENTION INDICES OF SOME SILANE AND DIPHENYL DERIVATIVES

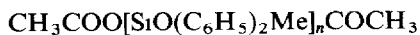
Chromatographed compound	Boiling point (°C)	Retention index		
		Dexsil-300	KBS-2	Silbor-1
Diphenyl	254	1497	1488	1638
<i>m</i> -Chlorodiphenyl	—	1616	1613	1788
<i>p</i> -Chlorodiphenyl	290	1708	1723	1883
Diphenyldiethoxysilane	304	1771	1808	1933
Diphenylchlorosilane	304	1865	1875	2029
Diphenyldixylenoxysilane	400	3025	3111 (400°C)	3518 (350°C)

TABLE 9^{1,2}
EFFECT OF THE SOLID SUPPORT ON RETENTION INDICES
Column, 150 × 0.4 cm I.D., temperature, 100°C

Solid support	10% Squalane			10% Polyethylene glycol 400								
	Hexa- none-2	Chloro- benzene	Penta- nol-1	2-Methyl- pentanone	Benzon- trile	Nitro- benzene	Hexa- none-2	Chloro- benzene	Penta- nol-1	2-Methyl- pentanone	Benzo- nitrile	Nitro- benzene
Chromosorb W	774.0	825.7	800.0	939.6	918.6	1016.9	1147.1	1347.2	1252.9	1377.0	1644.4	1745.0
Celite	747.2	826.0	763.5	902.3	904.2	1009.7	1170.0	1369.4	1275.0	1397.9	1675.8	1779.4
Anachrom	733.3	826.8	714.9	885.2	896.5	1005.2	1177.9	1384.2	1383.5	1408.8	1696.8	1801.2
Chromosorb G	732.6	826.9	714.4	835.3	896.6	1005.4	1179.0	1381.2	1284.2	1409.2	1693.3	1798.2
Gas-Chrom Q Silanized	730.9	826.8	703.9	883.2	893.1	1004.3	1181.8	1386.6	1287.6	1414.9	1702.3	1810.5
Chromosorb G	728.7	826.5	694.9	883.8	893.9	1005.1	1186.4	1390.7	1293.0	1419.1	1709.0	1817.0
Max difference, (I_{\max})*	45	1.2	106	56	25	12	39	47	41	42	65	72

* (I_{\max}) = (I_{\max} (solid support A)) - (I_{\min} (solid support B))

Kirichenko *et al.*¹²⁴ recommend, for the analysis of high-boiling compounds, siloxanes with a molecular weight of 1500–2000, containing metals in the main chain and having the general formula



where Me = Be or Cr.

Turkeltaub *et al.*¹²⁵ prepared a methylsiloxane stationary phase by polymerization and polycondensation of dimethyldichlorosilane directly on the surface of a solid support. The resulting sorbent was used to separate oligomers of dimethyl polysiloxanes with molecular weights of up to 500¹²⁶.

Yevdokimov and Lobkov¹²⁷ obtained a porous sorbent of the Porapak Q type by curing a dimethyl polysiloxane gum with a molecular weight of $5 \cdot 10^5$ under ^{60}Co gamma radiation, followed by heating of the cured product. The resulting porous polymer had a specific surface area of 20–50 m²/g, with a size pore ranging from 35 to 550 Å and a thermal stability of 300°C

In recent years, Vigdergauz and co-workers have published the results of various experiments with colloidal sorbents as stationary phases. Interesting results concerning the chromatography of organometallic compounds on PMS-100–Aerosil colloidal systems were reported in a review by Kirsh *et al.*¹²⁸. For example, on a column with 6% of the PMS-100–Aerosil (2:3) colloidal system, the temperature of analysis of bis-arene complexes of chromium could be lowered from 200 to 150°C, compared with PMS-100 alone¹²⁹, which is extremely important in the analysis of unstable compounds.

9. EFFECT OF ADSORPTION PHENOMENA ON THE McREYNOLDS CONSTANTS OF STATIONARY PHASES

The McReynolds constants⁴⁵, characterizing the ability of the stationary phase to be involved in various types of intermolecular interactions, are based on the determination of the retention indices of chemical compounds of different structures. It is known^{130,131} that retention indices are greatly influenced by the type and batch of the solid support. For example, Table 9¹³² lists the retention indices of some polar compounds on squalane and polyethylene glycol 400, which shows that on different supports the difference between the retention indices of the same substances may be as high as 50–100 units. Table 10¹³³ shows the results of measurements, in five different laboratories, of the retention indices of some hydrocarbons and chloroalkanes on squalane using different batches of the solid support Chesaorb. In this instance, the spread of retention indices is large, *i.e.*, up to 38 units.

The effect of the solid support on the retention indices of McReynolds test compounds was studied earlier⁴⁴ (Table 11). In other work¹³², the greatest differences were observed with non-silanized supports, especially Chromosorb, although the spread of the retention indices for compounds belonging to the same class (hexanone-2 and pentanone-2, pentanol-1 and butanol-1) was considerably smaller than that reported¹³² and did not exceed 16 units.

The data suggest that it is necessary to take into account the adsorption of the sample compounds if the retention values corresponding only to their dissolution in

TABLE 10¹³³

INTER-LABORATORY MEASUREMENTS OF RETENTION INDICES

Column, 200 × 0.3 cm, 6% squalane on Chesasorb, temperature, 70°C

Compound	Laboratory No					$(\Delta I)_{\max}^*$
	1	2	3	4	5	
<i>cis</i> -4-Methyl-pentene-2	561	565	563	562	—	4
Chloroform	589	595	600	597	—	11
Benzene	660	670	634	653	—	36
Dichloroethane	648	679	657	648	641	38
Heptene-1	686	688	687	684	687	4
Toluene	764	783	765	772	773	19

$$* (\Delta I)_{\max} = I_{\max}(\text{lab A}) - I_{\min}(\text{lab B})$$

the stationary phase are to be determined. The methods for such determinations were proposed by Berezkin¹³⁰ and are based on finding the invariant retention values from the equation

$$I_i = I_{0i} + \lambda_i/P$$

where

$$I_{0i} = 100z + 100 \log K_{1i}/K_{1z} / \log K_{1(z+1)}/K_{1z}$$

λ_i is a constant and P is the percentage of the stationary phase on the solid support (solid support weight = 100%). Note that in this equation the reciprocal of the stationary phase content may not only be the reciprocal of the percentage content of the stationary phase on the solid support, but also the reciprocal of the stationary phase volume in the column, the effective thickness of its film on the solid support or the reciprocal of the capacity ratio of the compound whose adsorption can be ignored for the chromatographic system under consideration, by virtue of its smallness.

As the relationship between the retention index and the reciprocal of the stationary phase content is usually adequately described by the above linear equation in the coordinates $I_i - 1/P$, there is every reason to use such relationships for deriving the values of I_{0i} . I_{0i} may be referred to as the limiting or invariant retention index, which places emphasis on its independence of the solid support type. I_{0i} is a function not of the retention time of the sample compounds but of the constants of its distribution. Consequently, this quantity must be more stable in the experimental environment, and its use must substantially enhance the repeatability of the experimental results. A joint experimental programme undertaken by five laboratories has corroborated this hypothesis. Table 12¹³³ lists the invariant retention indices for some hydrocarbons, calculated using the above equation. It can be seen that the invariant retention indices are characterized by a much better repeatability than those measured directly. For example, the maximum spread of the invariant retention indices for different compounds varies from 1 to 7 units, whereas for retention indices

TABLE 11⁴⁴
EFFECT OF THE SOLID SUPPORT ON RETENTION INDICES

Column. 2.35 m \times 0.3 cm I D, 20% squalane + 0.1% Span 80; temperature, 120°C

Solid support	Retention index		Benzene		Butanol-1		Pentane-2		1-Nitropropane		Pyridine	
	Obtained	Difference from McReynolds constants	Obtained	Difference from McReynolds constants	Obtained	Difference from McReynolds constants	Obtained	Difference from McReynolds constants	Obtained	Difference from McReynolds constants	Obtained	Difference from McReynolds constants
Celite-545	645	+1	594	+4	631	+4	656	+4	704	+5		
Chromosorb W AW	656	+3	601	+11	635	+8	662	+10	715	+16		
Chromosorb W AW HMDS	652	-1	596	+6	628	+1	653	+1	706	+7		
Chromosorb G (5% squalane + 0.1% Span 80)	655	+2	602	+12	634	+7	661	+9	713	+14		
Chromatron N AW DMCS (batch No 80483)	653	0	590	0	627	0	655	+3	701	+2		
Chromatron N AW DMCS (batch No 80426)	653	0	591	+1	627	0	653	+1	700	+1		
Supelcoport (80-100 mesh)	653	0	591	+1	627	0	653	+1	700	+1		

TABLE 12^{1,3,3}INVARIANT RETENTION INDICES, I_{0i} , FOR SOME ORGANIC COMPOUNDS ON SQUALANE AT 70°C

Compound	Laboratory No					$(\Delta I_{0i})_{max}$
	1	2	3	4	5	
<i>cis</i> -4-Methylpentene-2	553	555	556	554	—	3
Chloroform	579	580	582	575	—	7
Benzene	640	641	642	640	—	2
Dichloroethane	600	600	605	600	601	5
Heptene-1	681	681	682	682	683	2
Toluene	750	750	750	750	749	1

measured in a traditional manner the spread is from 4 to 38 units. Hence the repeatability is improved by a factor of 4–5 when invariant retention indices are used.

A similar approach must also be used to determine the McReynolds constants. This will permit (1) the properties of the stationary phase to be defined, as opposed to those of the sorbent, and (2) improvement of the repeatability of the retention indices. It is therefore recommended that for determining the properties of stationary phases invariant Rohrschneider and McReynolds constants found from the equations

$$\frac{I_{0imn}}{100} = \frac{I_{0im} - I_{0in}}{100}$$

and

$$I_{0imn} = I_{0im} - I_{0in}$$

where I_{0imn} is the difference between the invariant maximum retention indices for a substance i and phases m and n and I_{0im} and I_{0in} are the invariant (maximum) retention indices for the substance i and stationary phases m and n , respectively, should be used. These invariant constants characterize only the properties of the stationary phase under investigation.

10 CONCLUSION

Since 1960, Soviet researchers have extensively investigated the chromatographic properties of polysiloxane materials intended for use as stationary phases. Emphasis has been placed on the development of new types of phases, and many patents have been granted. To facilitate interchangeability of the Soviet stationary phases, foreign analogues for Soviet polysiloxane stationary phases have been described.

In estimating the properties of stationary phases, and determining of important characteristics such as McReynolds/Rohrschneider constants and upper temperature limits, considerable attention has been paid to the careful purification of the phases and their conditioning, exclusion liquid chromatographic techniques being recom-

mended for establishing their properties and the transformations which they undergo. The determination of the chromatographic properties of stationary phases is based on the estimation of the contribution made by the adsorption of the sample compounds to the overall retention value, which permits the interfering effect of the solid support to be taken into consideration.

As far as future developments are concerned, more attention should be paid to ensuring uniformity of individual batches of polysiloxane stationary phases. Developments in capillary gas chromatography are also of great importance.

11 SUMMARY

Polysiloxane stationary phases developed and used in the Soviet Union are described in detail, probably for the first time in the Western literature. Materials comparable to those produced by Western specialty chromatographic suppliers are included; polysiloxanes particularly suitable for high-temperature use are available in the Soviet Union and comparable materials are not available elsewhere. The effect of adsorption on the determination of McReynolds constants of stationary phases is discussed.

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