Journal of Chromatography, 365 (1986) 19–25
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP.858

HIGH-TEMPERATURE STATIONARY PHASES BASED ON LADDER SILOXANE POLYMERS

I. P. YUDINA*, G. N. SEMINA and K. I. SAKODYNSKII
Institute of the Ministry of Chemical Industry, Moscow (U.S.S.R.)

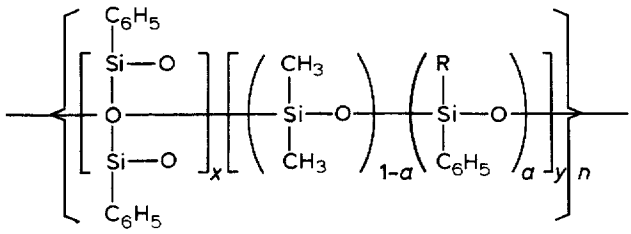
SUMMARY

The ladder-type siloxane polymer Lestosil has been investigated as a high-temperature stationary phase for gas chromatography. Its application to the separation of different classes of chemical compounds has demonstrated the possibility of selective separation of high-boiling polar compounds without converting them into more volatile derivatives.

INTRODUCTION

As part of our extensive work aimed at creating high-temperature selective stationary phases based on different modifications of siloxane polymers, the ladder-type siloxane polymer Lestosil[1] has been studied. This polymer had not been used before as a stationary phase. An investigation of its physical-chemical properties has shown that it may be employed as the basis of selective stationary phase which possess high thermal stability and, therefore, are capable of separating a number of high-boiling organic and organasilicon compounds.

Lestosil is a colourless sponge polymer soluble in chloroform, dichloromethane, benzene and toluene. It can withstand temperatures as high as 420°C (as judged by thermogravimetric analysis, TGA), 400°C according to FID data. Its macromolecule comprises cyclic siloxane tetrameric units incorporating phenyl groups at silicon (silsesquioxane) linked by linear siloxane chains containing dimethyl and methylphenyl groups (polydimethylphenylsiloxane)



where a = 0–0.33, R is CH_3 or C_6H_5, x = 6–60 and y = 10–350; MW 1000–30 000.

TABLE I

Mc REYNOLDS CONSTANTS FOR LESTOSIL AS A FUNCTION OF THE RATIO *y:x*

y:x	*X'*	*Y'*	*Z'*	*U'*	*S'*
5.6	65	110	120	160	168
2.8	79	126	190	184	262
2.0	102	170	151	211	239

The McReynolds constants were determined (at 120°C) as a function of the ratio *y:x* of the number of polydimethylphenylsiloxane units, *y*, to that of silsesquioxane units, *x* (Table I). From the values of the McReynolds constants it follows that the polymer polarity depends on *x* and *y* and their ratio, *y:x*, *i.e.*, the polarity of Lestosil may be regulated by introduction of a definite quantity of either silsesquioxane or polydimethylsiloxane (PDMS) with phenyl groups.

Table II illustrates the effect of the introduction of phenyl radicals into the PDMS linear chain on the polarity of various stationary phases[2,3]. As can be seen from Tables I and II, Lestosil, unlike linear polymers, exhibits a larger increase in polarity on introduction of phenyl radicals. This is most likely due to its structure.

From the values of the McReynolds constants it is concluded that the present stationary phase has some advantages: it can provide a selective analysis of different classes of compounds and displays specificity towards the separation of both aromatics (*X'*) and polar compounds (*Y'*, *Z'*, *U'*, *S'*).

No structural analogues of Lestosil as a stationary phase are known in the practice of gas chromatography.

EXPERIMENTAL AND RESULTS

In vestigations of Lestosil were carried out using a Perkin-Elmer Model 900 gas chromatograph with a flame ionization detector at different temperatures; temperature programming was also used. Lestosil was applied, from a solution of chloroform, to the Chromaton N-AW support (0.20–0.25 mm) in amounts from 5 to 20% (w/w). A 2 m × 3 mm I.D. stainless-steel column was employed.

Before operation, the column packed with sorbent was conditioned according to the following program: heated from 50 to 380°C at 4°C/min, after every 50° rise in temperature, carrier gas (helium) was passed for 2 h; at 380°C the carrier gas was

TABLE II

EFFECT OF PHENYL RADICALS ON THE POLARITY (McREYNOLDS CONSTANTS) OF VARIOUS STATIONARY PHASES

Phase	*Phenyl (%)*	*X'*	*Y'*	*Z'*	*U'*	*S'*	*Ref.*
SE-30	–	15	53	44	64	41	2
SE-54	5	33	72	66	99	67	2
OV-3	10	44	86	81	124	85	2, 3
OV-7	20	69	113	111	171	128	3
DC-550	25	74	116	117	178	135	2
OV-11	35	102	142	145	219	178	3

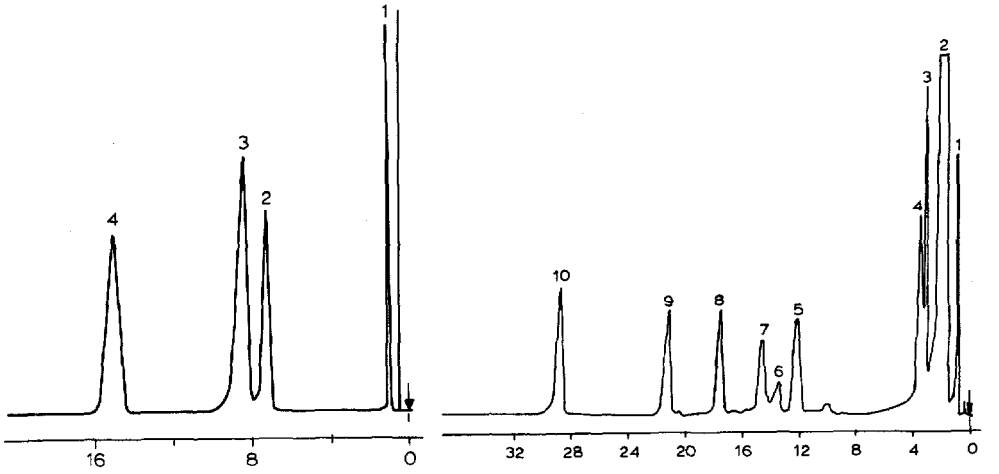


Fig. 1. Chromatogram of close-boiling compounds. Temperature: 100°C. Flame ionization detection. Peaks: 1 = cyclohexylamine; 2 = phenol; 3 = aniline; 4 = nitrobenzene.

Fig. 2. Chromatogram of impurities in commercial aniline. Temperature: 120°C for 8 min, then increased to 220°C at 4°C/min. Detection as in Fig. 1. Peaks: 1 = cyclohexylamine, 2 = aniline; 3 = nitrobenzene; 4 = toluidines; 5 = *o*-nitroanisole; 6 = *m*-phenylenediamine; 7 = biphenyl; 8 = N-phenylcyclohexylamine; 9 = diphenylamine; 10 = carbazole.

passed for 24 h. As a result, the column could be operated at high temperatures with highly sensitive detectors and no baseline drift.

Separations were performed of close-boiling compounds having the same num-

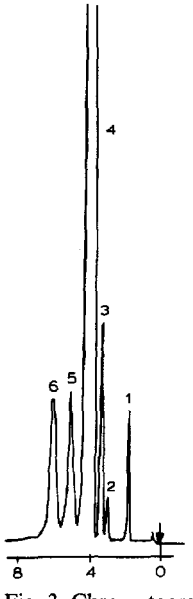


Fig. 3. Chromatogram of commercial 2-aminoanisole (*o*-anisidine). Temperature: 150°C. Detection as in Fig. 1. Peaks: 1 = aniline; 2 = *o*-chloroaniline; 3 = N-chloroaniline; 4 = *o*-anisidine; 5 = n-anisidine; 6 = *o*-nitrochlorobenzene.

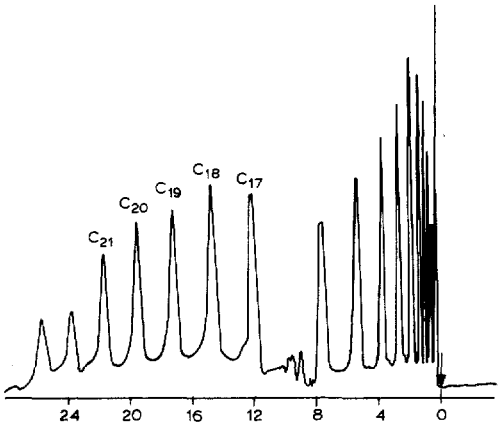


Fig. 4. Chromatogram of C_{17}–C_{21} amines. Temperature: programmed from 180 (8 min) to 250°C at 4°C/min. Detection as in Fig. 1.

ber of carbons, *i.e.*, C_6 (cyclohexylamine, phenol, aniline and nitrobenzene), Fig. 1. The successful separation of cyclic amines from aromatic amines (cyclohexylamine from aniline), alcohols from amines, nitro compounds from amines and alcohols testifies to the high specificity of this phase towards these classes of compounds. For this reason the phase may be recommended for the analysis of commercial products which very often represent complex mixtures of compounds of different classes.

A commercial aniline produced by catalytic reduction of nitrobenzene was

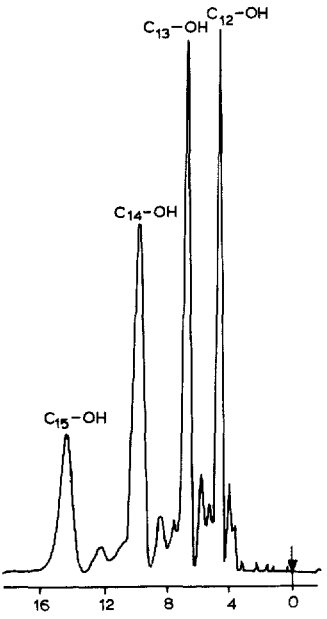


Fig. 5. Chromatogram of C_{12}–C_{15} alcohols produced in the oxo process. Temperature: 170°C. Detection as in Fig. 1.

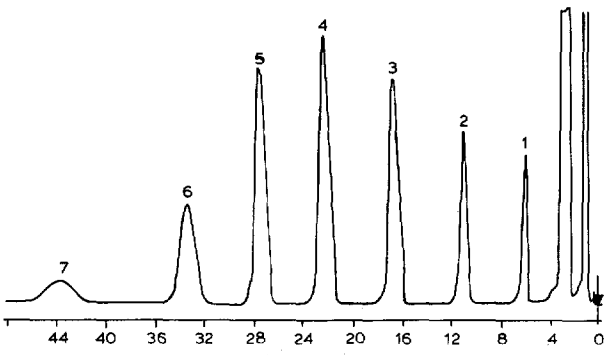


Fig. 6. Chromatogram of polypropylene glycol (PPG-250). Temperature: programmed from 150 to 280°C at 4°C/min. Detection as in Fig. 1. Peaks: 1 = monopropylene glycol; 2 = dipropylene glycol; 3 = tripropylene glycol; 4 = tetrapropylene glycol; 5 = pentapropylene glycol; 6 = hexapropylene glycol; 7 = heptapropylene glycol.

chromatographed and the following impurities were identified: cyclohexylamine, nitrobenzene, toluidines, *o*-nitroanisole, *m*-phenylenediamine, biphenyl, N-phenylcyclohexylamine, diphenylamine and carbazole. An effective separation was achieved of cyclic, aromatic and cycloaromatic amines boiling over a wide temperature range from 180 to 360°C (Fig. 2).

Impurities in commercial 2-aminoanisole (*o*-anisidine) were identified (Fig. 3).

It should be noted that the separation of the above commercial mixtures was achieved without preliminary sample treatment, which is commonly applied in chromatographic analysis of amino compounds; the peaks of these polar compounds were symmetric.

This suggested that the phase could be used for separation of homologous series of C_{17}–C_{21} amines; Fig. 4 shows that symmetric peaks were obtained in a temperature-programmed analysis from 180 (8 min) to 250°C.

The specificity of the phase was also demonstrated by separation of C_{12}–C_{15}

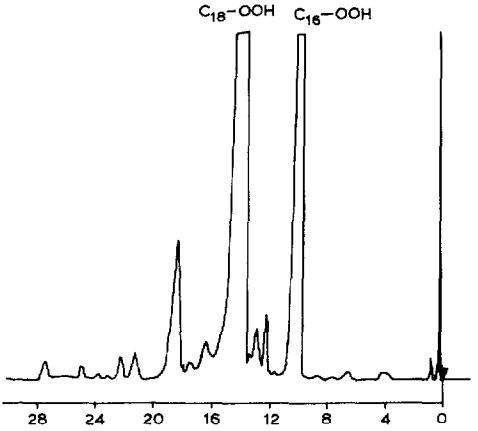


Fig. 7. Chromatogram of commercial C_{16}–C_{18} fatty acids. Temperature: programmed from 150 to 270°C at 4°C/min. Detection as in Fig. 1.

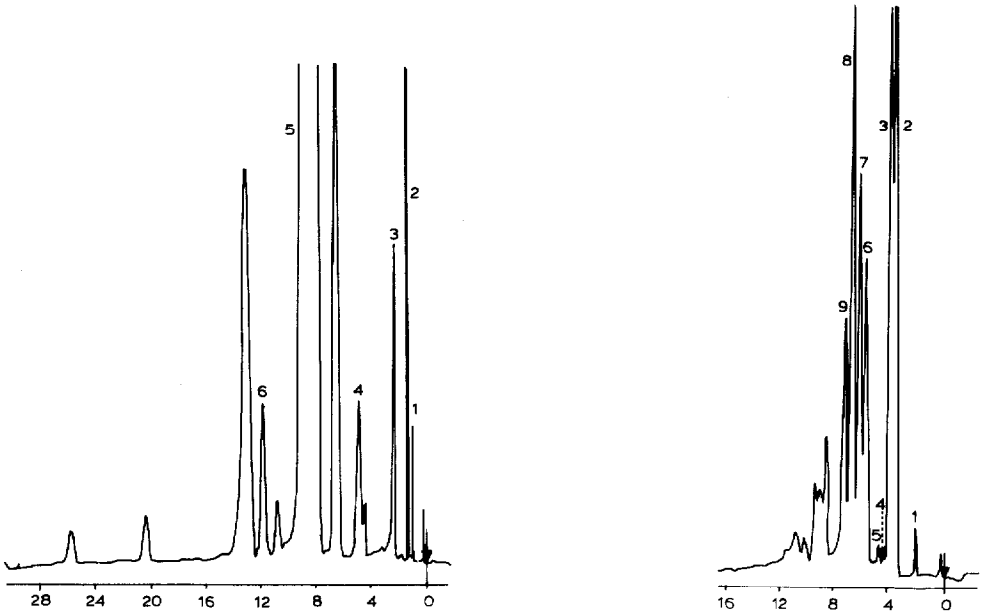


Fig. 8. Chromatogram of commercial diethylaminoethyl methacrylate. Temperature: programmed from 180 to 220°C at 4°C/min. Detection as in Fig. 1. Peaks: 1 = methyl methacrylate; 2 = toluene; 3 = diethylethanolamine; 4 = monoethyl acrylate ethylene glycol; 5 = diethylaminoethyl methacrylate; 6 = dimethacrylate ethyleneglycol.

Fig. 9. Chromatogram of commercial isopropylbiphenyl. Conditions as in Fig. 8. Peaks: 1 = biphenyl; 2 = 3-isopropylbiphenyl; 3 = 4-isopropylbiphenyl; 4 = 3-propylbiphenyl; 5 = 4-propylbiphenyl; 6 = 3,5-diisopropylbiphenyl; 7 = 3,3′-diisopropylbiphenyl; 8 = 3,4-diisopropylbiphenyl; 9 = 4,4′-diisopropylbiphenyl.

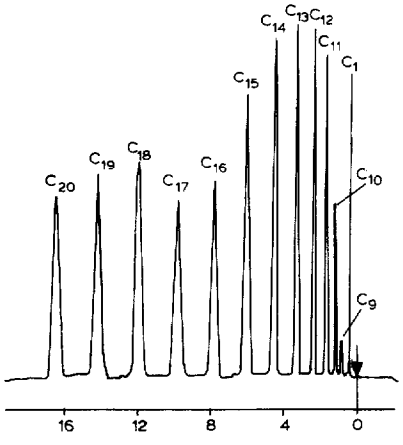


Fig. 10. Chromatogram of C_6–C_{20} hydrocarbons. Temperature: programmed from 150 to 220°C at 4°C/min. Detection as in Fig. 1.

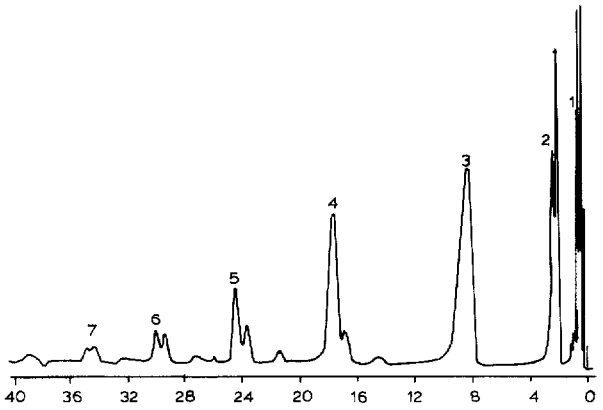


Fig. 11. Chromatogram of commercial ethyl silicate ES-32. Temperature: programmed from 150 (8 min) to 300°C at 4°C/min. Detection as in Fig. 1. Peaks: 1 = ethanol; 2 = tetraethoxysilane; 3 = ethoxydisiloxane; 4 = ethoxytrisiloxane; 5 = ethoxytetrasiloxane; 6 = ethoxypentasiloxane; 7 = ethoxyhexasiloxane.

alcohols produced by the oxo process (Fig. 5), polypropylene glycol of MW 250 (Fig. 6) and commercial C_{16}–C_{18} fatty acids (Fig. 7). A complete separation of high-boiling polar compounds was attained without converting them into more volatile derivatives, and their peaks were symmetric.

The high thermal stability and selectivity of Lestosil is also exemplified by the separation of high-boiling components of diethylaminoethyl methacrylate (Fig. 8). Further evidence of the specificity was provided by the separation of commercial isopropylbiphenyl where a good separation of biphenyl isomers was achieved (Fig. 9).

A good separation of C_6–C_{20} hydrocarbons, which are non-polar compounds, was also achieved (Fig. 10).

Finally, the stationary phase was applied to the separation of organosilicon compounds, *e.g.*, ethyl silicate ES-32, an industrial product employed in producing high-purity silicon oxide (Fig. 11). The chromatogram obtained makes it possible to estimate the composition of the ethyl silicate binder and determine the amount of ethanol formed in the process.

Thus it may be concluded that the stationary phase Lestosil provides a high-temperature selective analysis of different classes of organic and organosilicon compounds. Noteworthy are the high selectivity, separating power and efficiency of Lestosil together with its high thermal stability. For this reason Lestosil may be useful in analyzing mixtures of high-boiling compounds under conditions of temperature programming up to 400°C, the detector sensitivity being unaffected. It is also to be noted that the separation of polar compounds, such as amines, alcohols and fatty acids, is possible without their pretreatment, and the stationary phase does not loose its high thermal stability.

REFERENCES

1 A.C. No. 1056050 (USSR), *Bul. Inventions*, No. 43, November 23, 1983.
2 *Analabs Catalogue*, 1980, N 20.
3 *International Chromatography Supplies Catalogue*, 1982, N 16.