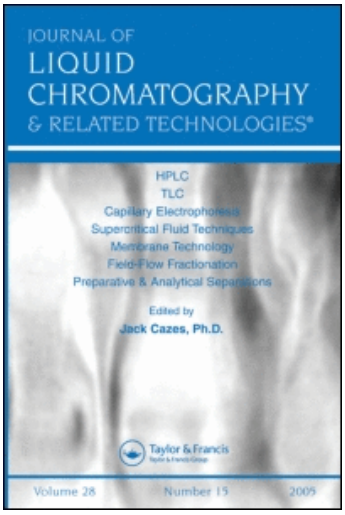


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# SEPARATION AND DETERMINATION OF ALKYLFURYLSILANE ISOMERS FOR HPLC

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□ *In this paper are presented optimal conditions of chromatographic separation of two isomers: γ-(chloropropyl)-3-furyldimethylsilane and [2-chloro(1-methyl)ethyl](3′-furyl)dimethylsilane. These isomers show the ability of modification of the surface of silica gel. In the investigation were tested three stationary phases and three mobile phases: dichloromethane, methanol, and a mixture of dichloromethane and hexane (80/20, v/v), in different flow intensities. An application of octadecyl stationary phase, which is recommended as a standard phase, did not yield separation of the isomers, independently of composition and flow of a mobile phase. Better results, but with asymmetric peaks have been obtained on the octyl phase. Finally, aryl chemically bonded phases permitted acquiring good separation of the isomers in a time shorter than 25 min. The best separation factor (1.11) has been obtained on the chemically bonded aryl phase using dichloromethane with flow of* $0.1\,mL \cdot min^{-1}$. *Therefore, the best selectivity in separation of above mentioned compounds exhibited the aryl chemically bonded phase.*

**Keywords** aryl, 3-furylsilanes, isomers, octadecyl, octyl, stationary phases

## INTRODUCTION

Furylsilane compounds substituted in position 2 have been known for a few dozen of years, and it is common knowledge that they are exhibiting biological activity.[1] Slightly less known are analogous compounds substituted in position 3. The first synthesis of this group was carried out in Riga.[2]

Now, after preliminary tests, they are also supposed to be biologically active. However, not much information is accessible concerning their chromatographic separation and determination. First of all, it is caused by difficulties connected with chromatography of these compounds.

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Unfortunately, many of them can not be separated or determined using standard, $C_{18}$ columns. Usually, they have a long retention time of more than 60 min and this fact discourages an analyst from elaborating a process of separation and analysis.

Furylsilanes are a group of compounds, which should be analysed or separated by means of so called dedicated stationary phase. An example of such phase is the aryl chemically bonded stationary phase (phenylbutyl). A lack of free silanol groups on the silica surface and the presence of $\pi$-electrons in the phenyl substituent cause additional interaction between the chromatography compound and the stationary phase. Thanks to this interaction, good separation and analysis can be observed in numerous chromatographic processes.[3–6] In particular, aryl phases are dedicated to separation and analysis of compounds containing an aromatic ring, e.g., polycyclic aromatic hydrocarbons (PAHs).

Synthesis of the first so called dedicated phases started in 1989, when Pidgeon proposed a new generation of packing intended for biochemical separation of immobilised artificial membranes (IAM).[7] Later Buszewski and coworkers successfully applied these for separation of amines, proteins, alkaline medicines, and PAHs of various stereogeometry.[8–11] Well known are also cyclodextrine phases introduced by Armstrong and coworkers.[12] Success also was achieve with phases containing chiral active centres, so called phases of Pirkle's type ($\pi$-donor, $\pi$-acceptor).[13,14]



Because properties of a group of furylsilane compounds substituted in the position 3 are not sufficiently known and methods of their chromatographic determination are not described, the aim of our investigation seems to be justified. The main task of this investigation was elaborating optimal conditions of chromatographic separation and determination of two isomers: $\gamma$-(chloropropyl)-3-furyldimethylsilane and [2-chloro(1-methyl)ethyl](3′-furyl)dimethylsilane by means of high performance liquid chromatography method.

## EXPERIMENTAL

### Materials and Method

Aforementioned isomers were prepared according to published procedure:[2] $\gamma$-(chloropropyl)-3-furyldimethylsilane (furyl.1) and [2-chloro(1-methyl)ethyl](3′-furyl)dimethylsilane (furyl.2) (Fig. 1) were dissolved in dichloromethane (HPLC purity, Fluka AG, Buchs, Switzerland). Concentration of the samples was at about 15 $\mu g \cdot mL^{-1}$. The samples were directly subjected to HPLC analysis, at wavelength 265 nm and temperature 20°C. In the investigation, three stationary phases were used: octadecyl (RP Si–$C_{18}$), octyl (RP Si–$C_8$) and aryl (RP Si–PB, Figs. 2 and 3, Table 1).[11]

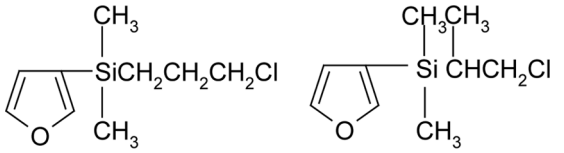


**FIGURE 1** Structures of 3-furylsilane isomers: (a) furyl.1, and (b) furyl.2.

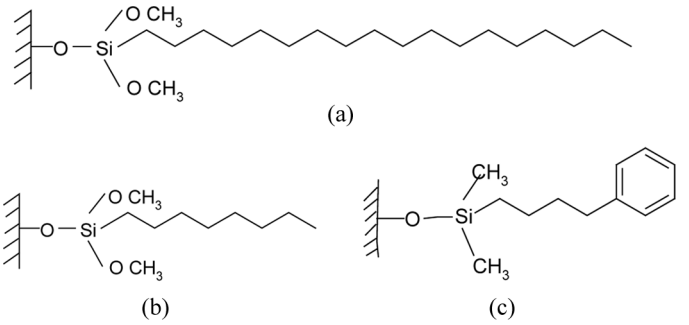


**FIGURE 2** Scheme of chemically bonded stationary phases: (a) octadecyl, (b) octyl, and (c) phenylbutyl.



A strong anhydrous eluent had to be used, because these compounds were very slowly leaving columns. Therefore, applied systems were: dichloromethane and methanol, with flow 0.5, 0.3, and 0.1 mL · min$^{-1}$, in turn (Table 2). (Additionally, a mixture of dichloromethane and hexane

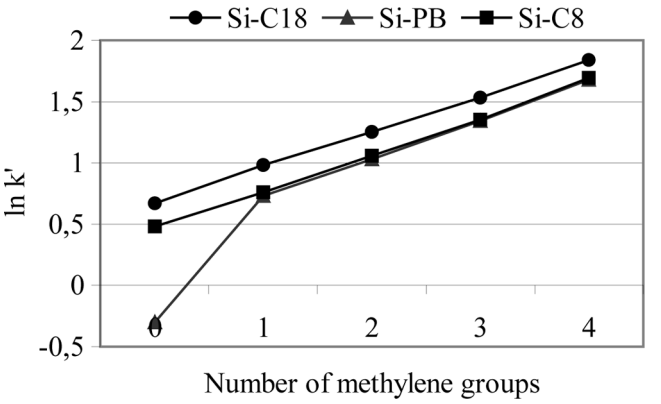


**FIGURE 3** Dependence ln k′ on the number of carbon atoms in alkyl chain of alkyl-benzenes for octyl, octadecyl and phenylbutyl packings. Chromatographic conditions: mobile phase 65/35 vol.% acetonitrile/water, flow rate – 1 mL · min$^{-1}$, wavelength – 254 nm, temperature – 20°C.

**TABLE 1** Characteristics of Bonded Phase

| Type of Packing | Manufacturer of Column | Dimensions of Column [mm] | Carbon Content vol. % |
|---|---|---|---|
| Octadecyl | S. Witko–J. T. Baker | 250 × 4.6 | 18.09 |
| Octyl | Home made | 125 × 4.6 | 13.49 |
| Phenylbutyl | Home made | 125 × 4.6 | 14.9 |

(80/20, v/v), but without success). Separated by this method, furylsilyl isomers were identified using $^{1}$H NMR and $^{13}$C NMR. The furylsilane isomers compounds were prepared by the method described in the literature.[2]

$\gamma$-(chloropropyl)-3-furyldimethylsilane: $^{1}$H NMR (DMSO), $\delta$ (ppm): 0.48 (6H; $CH_3$), 0.9–1.0 (2H; $SiCH_2$), 1.50–1.73 (2H; $CCH_2C$), 3.46 (2H; $CCH_2Cl$), 6.1 (1H; H-4), 7.1 (1H; H-2), 7.23 (1H; H-5). $^{13}$C NMR (DMSO), $\delta$ (ppm): 1.33 ($CH_3$), 9.4 ($SiCH_2$), 27.32 ($CCH_2C$), 47.9 ($CCH_2Cl$), 120.2 (C-4), 141.77 (C-5), 147.0 (C-2), 147.6 (C-3).

UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\lg \varepsilon$) = 241 (2.38), 265 (2.42), 291 (2.46).

[2-chloro(1-methyl)ethyl](3′-furyl)dimethylsilane: $^{1}$H NMR (DMSO), $\delta$ (ppm): 0.35 (6H; $CH_3$), 1.11 (3H; $CH_3$), 1.31–1.43 (1H; CH), 3.48–3.60 (2H; $CCH_2Cl$), 6.1 (1H; H-4), 7.1 (1H; H-2), 7.15 (1H; H-5). $^{13}$C NMR (DMSO), $\delta$ (ppm): 6.92 ($SiCH_3$), 14.56 ($CH_3$), 22.50 (CH), 46.70 ($CCH_2Cl$), 123.52 (C-4), 137.99 (C-3), 141.77 (C-5), 146.85 (C-2).

UV/Vis ($CH_2Cl_2$): $\lambda_{max}$ ($\lg \varepsilon$) = 242 (2.38), 265 (2.42), 291–292 (2.46).



**TABLE 2** Chosen Dependence $\ln k'$ for Furyl.1 and Furyl.2 from on Type of Stationary and Mobile Phase. Chromatographic Conditions: Flow – 0.3 or 0.1 mL · min$^{-1}$, Wavelength – 265 nm, Temperature – 20°C

| Type of Stationary Phase | Mobile Phase*/Flow Rate [mL · min$^{-1}$] | $k'_1$ | $k'_2$ | $\alpha = k'_2/k'_1$ |
|---|---|---|---|---|
| RP Si–$C_{18}$ | Dichloromethane/0.3 | 26.64 | 26.64 | 1.00 |
| | Dichloromethane/0.1 | 45.55 | 45.56 | 1.00 |
| | Methanol/0.3 | 29.69 | 29.70 | 1.00 |
| | Methanol/0.1 | 48.71 | 48.89 | 1.00 |
| RP Si–$C_8$ | Dichloromethane/0.3 | 17.03 | 18.37 | 1.07 |
| | Dichloromethane/0.1 | 25.92 | 27.13 | 1.05 |
| | Methanol/0.3 | 19.98 | 21.14 | 1.06 |
| | Methanol/0.1 | 30.11 | 31.26 | 1.04 |
| RP Si–PB | Dichloromethane/0.3 | 11.61 | 12.67 | 1.09 |
| | Dichloromethane/0.1 | 19.43 | 21.53 | 1.11 |
| | Methanol/0.3 | 12.21 | 13.12 | 1.07 |
| | Methanol/0.1 | 20.45 | 21.68 | 1.06 |

*In the table are presented only these data of isomer separation, which are concerning retention time shorter than 50 min.

### Apparatus

$^{1}H$, $^{13}C$ NMR spectra were recorded on a Varian Mercury 400 MHz in DMSO, with TMS as internal standard. The UV/Vis spectra were recorded on a spectrophotometer DU-68 (Beckman, USA).

Chromatographic measurements were performed on a liquid chromatograph SPD-6A (Shimadzu, Kyoto, Japan) equipped with a pump LC-6A, UV detector, a sampling valve Rheodyne (Berkeley, CA, USA), model 7125, with a 20 μL sample loop, and a Shimadzu C-R6 A data recorder. The obtained chromatogram was recorded by the use of OriginPro 7.5 program (OriginLab Corporation, Northampton, USA).

## RESULTS AND DISCUSSION

Optimal conditions of separation and determination of two newly synthesised furylsilane derivatives have been elaborated. Obtained results are presented in Table 2. Looking for the best conditions of the chromatographic process, various compositions of the mobile phase and three stationary phases: octadecyl, octyl, and aryl (i.e., phenylbutyl) were taken into consideration. Octadecyl stationary phase is often recommended as the standard and most frequently used. Octyl phase is applied somewhat rarer. These phases are sometimes not sufficient to ensure satisfactory separation of determined compounds.



More and more often to complete separation of numerous groups of compounds, so called dedicated stationary phases are used,[12–16] as an example, aryl (phenylbutyl) chemically bonded stationary phase. Table 1 and Figs. 2 and 3 presents profiles of this phase.[11] The phase is characterised by the fact, that in the chromatographic process, besides normally existing interactions between the alkyl chain and analysed compound, interactions of $\pi$–$\pi$ type appear. Due to these interactions, separation of numerous isomers, their determination and shortening of retention time of analysed compounds, became possible. The same effect, shown in Table 2 and Figs. 4–6, also enabled obtainimg a good separation of analysed isomers, furylsilane derivatives.

Optimisation of the separation of isomer furyl.1 and furyl.2 by means of RP Si–$C_{18}$ was unfortunately unsuccessful, despite using different mobile phases and different flow rates. Unsatisfactory, separation was obtained by the use of octyl column (Figs. 4 and 5) because of shape and symmetry.

The aryl column (RP Si–PB) was characterised by the best separation of the above mentioned isomers and the shortest time of their retention. Optimal separation (separation factor $\alpha = 1.11$) on this column was achieved for the mobile phase consisting of 100% dichloromethane and flow $0.1\,mL \cdot min^{-1}$ (Fig. 6). Retention time of analysed compounds was

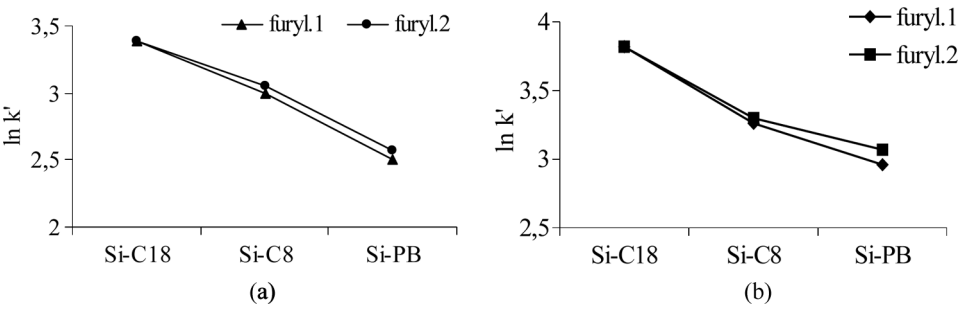


**FIGURE 4** Effect of the separation of furyl.1 and furyl.2 with the use of stationary phases RP Si–$C_{18}$, RP Si–$C_8$ and RP Si–PB. Mobile phase: (a) methanol (vol. 100%), flow rate: 0.3 mL · $min^{-1}$, (b) dichloromethane (vol. 100%), flow rate: 0.1 mL · $min^{-1}$, detection – 265 nm (see Table 2).

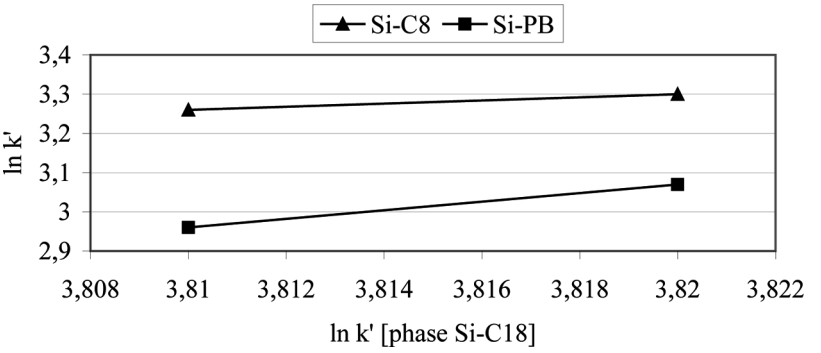


**FIGURE 5** Dependence of ln k′ of the RP Si–$C_8$ and RP Si–PB phases on ln k′ obtained for the octadecyl phase for furyl.1 and furyl.2.

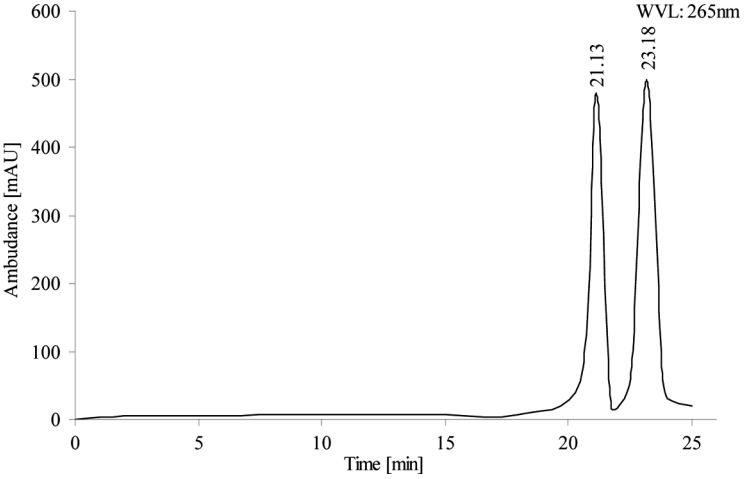


**FIGURE 6** A chromatogram of separation of the furyl.1 (21.13 min) and furyl.2 (23.18 min) on the stationary RP Si–PB phase. Mobile phase: dichloromethane (vol. 100%); flow – 0.1 mL · $min^{-1}$, wavelength – 265 nm, temperature – 20°C.

21.13 min for furyl.1 and 23.18 for furyl.2. Similarly proportional results were obtained when other systems of the mobile phase were applied. Data for water containing systems and dichloromethane-hexane mixture are not presented because of long retention time, over 60 min, and peak asymmetry. Other data concerning separation of aforementioned compounds by three stationary phases are shown, in the form of capacity factors k′, in Table 2.

Optimisation of separation conditions of discussed isomers, i.e., γ-(chloropropyl)-3-furyldimethylsilane and [2-chloro(1-methyl)ethyl](3′-furyl) dimethylsilane, according to data presented in Table 2, showed that independently of a composition and kind of the mobile phase, phenylbutyl chemically bonded stationary phase RP Si–PB is characterised by the best selectivity. Significantly longer retention times, compared with RP Si–PB phase and asymmetrical peaks were obtained, using phase RP Si–$C_8$. However, the use of octadecyl stationary phase, which is recommended as a standard phase, did not yield separation of the analysed isomers, independently of composition and flow of a mobile phase.



## CONCLUSIONS

In order to achieve good chromatographic separation of isomers: γ-(chloropropyl)-3-furyldimethylsilane and [2-chloro(1-methyl)ethyl](3′-furyl)dimethylsilane in the possible shortest time, an application of aryl chemically bonded stationary phase is recommended. The octadecyl stationary phase, which by many analysts is considered as a standard phase, did not yield separation of the analysed isomers. The octyl phase allowed obtaining partial separation, but the shape of peaks is not in accordance with the so called Gauss's curve.

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