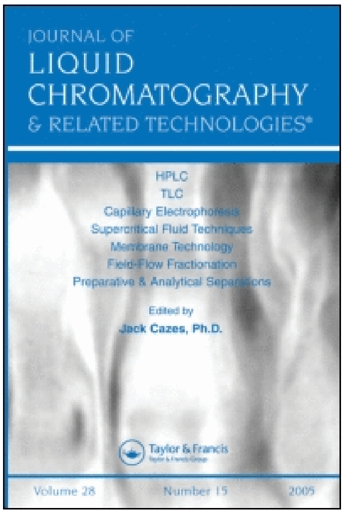

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Silica Based Aminopropyl-Bonded Phase Trimethylsilylated with N-Trimethylsilylimidazole

B. Porsch[a]
[a] Institute of Macromolecular Chemistry Czechoslovak Academy of Sciences, Czechoslovakia

To cite this Article Porsch, B.(1991) 'Silica Based Aminopropyl-Bonded Phase Trimethylsilylated with N-Trimethylsilylimidazole', Journal of Liquid Chromatography & Related Technologies, 14: 1, 71 — 78
To link to this Article: DOI: 10.1080/01483919108049598
URL: http://dx.doi.org/10.1080/01483919108049598

JOURNAL OF LIQUID CHROMATOGRAPHY, 14(1), 71-78 (1991)

SILICA BASED AMINOPROPYL-BONDED PHASE TRIMETHYLSILYLATED WITH N-TRIMETHYLSILYLIMIDAZOLE

B. PORSCH
Institute of Macromolecular Chemistry
Czechoslovak Academy of Sciences
CS-162 06 Prague 6, Czechoslovakia

ABSTRACT

N-trimethylsilylimidazole is a suitable agent for the silanization of silica based amino phases, because it reacts selectively with silanol groups. The effect of trimethylsilylation is illustrated chromatographically in anhydrous heptane and in separations of sugar mixtures in the acetonitrile-water mobile phase.

INTRODUCTION

An almost exclusively used procedure of preparation (1) of silica based bonded phases are reactions of halogen or alkoxysilanes containing the selected functional group with surface silanol groups in an anhydrous medium. Irrespective of the silane used (tri, di, monochloro, or alkoxy), the resulting product always contains residual silanol groups (unreacted for steric reasons or secondary, arising by the hydrolysis of unreacted alkoxyl or halogen). This is why additional trimethylsilylation, which effectively blocks these silanol groups, is regarded as one of the operations which determine the final properties of bonded phases. Also, it has the decisive influence on the usefulness of reverse phases (2), where the aim consists in a modified hydrophobization of the surface, because residual silanols are of opposite character. On the contrary, although for polar bonded phases one may expect changed chromatographic properties after trimethylsilylation, it cannot be a priori decided whether the replacement of residual silanols with a nonpolar group would mean a change for the better.

Silica with a chemically bonded primary amino group can be trimethylsilylated (2) similarly to the reverse phase (3) (usually, with trimethylchlorosilane, hexamethyldisilazane or a mixture thereof); at the same time, the amino group is also silylated (2,4). Trimethylsilyl amines are readily hydrolyzed with water (2,4,5), but a question remains if the hydrolysis will proceed quantitatively also on the sorbent's surface. In gas chromatography N-trimethylsilylimidazole, which is known (5) not to react with aliphatic amino groups, is used in the selective silylation of hydroxyl groups along with the amino group.

In this study we compare the unsilanized and silylated with trimethylsilylimidazole amino phase in its most usual application, i.e. in the chromatograpic analysis of sugar mixtures. Also, we examine the effect of trimethylsilylation on the chromatographic behaviour of this phase in an anhydrous medium.

EXPERIMENTAL

Separon SIX NH_2, particle size $d_p = 10 \mu m$, was manufactured (present manufacturer Tessek Ltd, Prague) by Laboratory Instruments, Prague. The reference amino phase was prepared in boiling toluene (4) by reacting γ-aminopropyltriethoxysilane (Petrarch Systems Inc., USA) with spherical silica Separon SIX (d_p = 10μm, Laboratory Instruments, Prague; present manufacturer Tessek Ltd, Prague). N-trimethylsilylimidazole (pure, Fluka AG, Buchs, Switzerland) was used directly. The solvents used - toluene, methanol, dioxan (Lachema, Brno), n-heptane (Fluka AG) and acetonitrile (Croft Laboratories Brackley, England) were reagent grade. Xylose, arabinose, fructose, glucose, saccharose, maltose, lactose, nitrobenzene, o-, m-, p-chloronitrobenzenes were made by Fluka AG.

The liquid chromatograph consisted of a reciprocal membrane pump VCM 300 (Development Workshop, CSAS, Prague), a stop-flow injection device made at the Institute, a differential refractometer R 401 (Waters Assoc., Milford, M.A., USA) or a UV detector LCD 254 (Laboratory Instruments, Prague) and a recorder Servogor 2S (Goerz Electro, Vienna, Austria). Stainless steel columns 100 × 6 mm I.D. made at the Institute were slurry packed in a methanol-dioxan mixture at 40 MPa.

Trimethylsilylation was carried out by reacting the respective amino phase with a 20% solution of N-trimethylsilylimidazole (in a fourfold excess related to the number of silanol groups of the starting silica) in toluene at 45°C and 60°C for 6 h with shaking in a shaker in a drying box.

The content of amino groups was determined by acidobasic titration with perchloric acid in anhydrous acetic acid (6).

RESULTS AND DISCUSSION

A comparison between the content of the organic phase and of primary amino groups before and after trimethylsilylation can be seen in Table 1. In both cases there is a considerable increase in the carbon content (2.2% at 60°C

TABLE 1

Additional Silanization of the Silica Based Primary Amino-Bonded Phase with N-Trimethylsilylimidazole

Sorbent	Elemental analysis			NH_2 content
	% C	% H	% N	mmol/g
I[a]	8.16	1.92	1.88	1.20
SIX NH_2[b]	5.96	1.52	1.97	1.36
II[c]	6.66	1.68	1.75	1.19
SIX NH_2[d]	5.43	1.54	1.80	1.27

[a] 60°C

[b] starting amino phase prepared with boiling in toluene from Separon SIX

[c] 45°C

[d] starting amino phase, commercial sample Separon SIX NH_2

and 1.3% at 45°C). The decrease in the content of amino groups is related with this increase. Let it be mentioned that after an intensive trimethylsilylation of unmodified silica the carbon content in the sorbent increases up to 6% (4).

The effect of trimethylsilylation on chromatographic properties was characterized by chromatographing nitrobenzene and isomeric chloronitrobenzenes in anhydrous heptane. Changes in the k' value of nitrobenzene should reflect (7) the change in the content and activity of silanol groups on the sorbent's surface: in Table 2 we can see that indeed the k' value of nitrobenzene decreases after trimethylsilylation, the more so the higher the degree of silylation. Good resolution and the corresponding order of separation of isomeric chloronitrobenzenes are typical of the amino phase; the cyanoethylated silica gel with a similar content of the organic phase separates the m- and p-isomer much more poorly and in a reversed order (8). Table 2 shows that after trimethylsilylation both the order and the good selectivity (as the separation factor $\alpha = k'_{para}/k'_{meta}$ of the isomer) remain, so that it

TABLE 2

A Comparison of Chromatographic Properties of Separon SIX NH_2 before and after Trimethylsilylation in Dry Heptane

Sorbent	Nitrobenzene k'	k', chloronitrobenzenes para	meta	ortho	α p/m isomer
I	1.40	0.98	1.24	2.67	1.26
SIX NH_2	2.80	2.67	3.73	8.94	1.40
II	1.79	1.21	1.70	3.86	1.40
SIX NH_2	2.83	1.79	2.63	6.05	1.47

may be concluded that the silylation of the amino group really does not take place. A slight drop in the α values and a decrease of k' of all the three isomers are in agreement with the assumed mechanism of separation (9) as a cooperative interation between silanols and the amino group on the one hand and the isomers under separation on the other, which also corresponds to the lower k' of nitrobenzene.

The application of amino phases most widely used are separations of sugars in acetonitrile/water as the mobile phase, where again the different selectivity of this sorbent is employed (10), as compared with the other normal phases based on silica gel. A typical example is e.g. the very good resolution of the pair glucose/fructose, which with other silica gels is difficult to achive (11). Table 3 summarizes differences in the behaviour of the amino phase before and after trimethylsilylation in the separation of mixtures of seven mono and disaccharides. It can be seen that in the polar mobile phase the effect of trimethylsilylation is not very strong. A slight decrease in the k' values can be observed only with a sample silylated at an elevated temperature, which can be explained by the fact that the introduction of hydrophobic groups brings about a decrease in the retention-determining water content in the stagnant liquid phase (12). Specific interations between the amino group and

TABLE 3

A Comparison of Chromatographic Properties of Separon SIX NH_2 before and after Trimethylsilylation in an Analysis of a Mixture of Sugars in the Mobile Phase Acetonitrile/Water = 80/20

Sorbent	k'							α		
	1 xylose	2 arabinose	3 fructose	4 glucose	5 saccharose	6 maltose	7 lactose	2/1	4/3	7/6
I	1.20	1.42	1.73	2.32	4.06	5.50	6.20	1.18	1.34	1.13
SIX NH_2	1.48	1.78	1.90	2.85	5.16	6.91	7.92	1.20	1.50	1.15
II	1.59	1.90	2.35	3.24	5.94	7.45	8.64	1.19	1.38	1.16
SIX NH_2	1.55	1.89	2.29	3.11	5.66	7.77	8.97	1.22	1.36	1.15

hydroxylic groups of sugars (10) probably determine selectivity (i.e. α), as confirmed by a comparison between the values in Table 3. The decrease in the α value observed with the strongly silylated sorbent is only small in the case of the pair glucose/fructose, and a less trimethylsilylated material cannot be distinguished from the starting material at all in this case. Similarly, in the amino phases with various contents of the bonded phase only the k' values of the surgars undergoing separation varied while selectivity remained virtually constant (13). The same ensues from data reported by Orth and Engelhardt (2).

The results obtained in this study confirm that N-trimethylsilylimidazole is a suitable agent for the selective trimethylsilylation of silanol groups on the surface of a chemically bonded primary amino phase. Although the trimethylsilylation of the amino phase did not result in better properties in the chromatography of mixtures of sugars, it raised the chromatographic stability of the amino phase (4). In special cases such as SEC of cation active polymers (14) the trimethylsilylated amino phase could become a suitable sorbent.

REFERENCES

1 Majors, R.E., Bonded-Phase Columns in HPLC, High Performance Liquid Chromatography Advances and Perspectives, Horváth, Cs., ed., Academic Press, N.Y., 1980, Vol.1, p. 76.

2 Orth, P. and Engelhardt, H., Chromatographia, 15, 91, 1982.

3 Melander, W.R. and Horváth, Cs., Reversed Phase Chromatography, High Performance Liquid Chromatography Advances and Perspectives, Horváth, Cs., ed., Academic Press, N.Y., 1980, Vol. 2, p. 114.

4 Engelhardt, H. and Orth, P., J. Liquid Chromatogr., 10, 1999, 1987.

5 Poole, C.F., Handbook of Derivatives for Chromatography, Blau, K. and King G.S., eds., Heyden and Son, London, U.K. 1976, Chapter IV, p. 152.

6 Cheronis, N.D. and Ma, T.S., Organic Functional Group Analysis, Interscience, N.Y., 1964.

7 Sander, L.C., J. Chromatographic. Sci., 26, 380, 1988.

8 Vivilecchia, R.V., Cotter, R.L., Limpert, R.J., Thimot, N.Z. and Little, J.N., J. Chromatogr.,99, 407, 1974.

9 Hammers, W.E., Spanjer, M.C. and DeLigny, C.L., J. Chromatogr., 174, 291, 1979.

10 Majors, R.E., J. Chromatographic Sci., 18, 488, 1980.

11 Aitzetmüller, K., J. Chromatogr., 156, 354, 1978.

12 Verhaar, L.A.Th., and Kuster, B.F.M., J. Chromatogr., 234, 57, 1982.

13 Porsch, B. and Krátká, J., J. Chromatogr., to be published

14 Wonnacott, D.M. and Patton, E.V., J. Chromatogr., 389, 103,1987.