Improvement of Biphenyl Sorbents by Bulky Substituents

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Introduction

Biphenylpropyl modified silica gels are an interesting alternative to octadecyl and octyl modified HPLC sorbents. Like C_8 or C_{18} alkyls, this ligand is sufficiently hydrophobic and chemically very inert. The conjugated π-system broadens the interactions between analyte and ligand by π–π interactions, so that the selectivity of this phase differs significantly from alkyl modified sorbents [1].

The biphenyl ligands are bound to the silica gel with siloxane bonds which are used in most HPLC phases. However, this siloxane bond can be hydrolyzed to a small extent at low pH values. Due to the strong absorption of UV light below 300 nm, biphenyl ligands can cause interfering signals using acidic conditions. This particularly affects fast gradients which are applied together with small silica particle sizes and core shell sorbents.

Bulky substituents can significantly improve the stability of the surface modification [2]. The influence of these substituents on stability and selectivity has been investigated.

Experimental

All stationary phases were prepared on core shell silica NUCLEOSHELL® 2.7 µm (MACHEREY-NAGEL). These sorbents were filled in stainless steel columns (100 mm x 3 mm) by a slurry packing method. Competitor columns were brand-new. For the chromatographic investigations, a Vanquish UHPLC system (Thermo Scientific) was used. All solvents are of HPLC grade.

Results

Under acidic conditions siloxane bonds are hydrolyzed (Fig 1). In the case of biphenyl-modified silica gels, this leads to interfering peaks at fast gradients under acidic conditions since biphenyl-containing compounds in the range of 200–300 nm strongly absorb UV light (Fig 2). The similarity of the UV spectra of eluate and allylbiphenyl demonstrates the presence of biphenyl-containing compounds in the eluate. As shown by Kirkland et al [2], the introduction of bulky substituents at the silicon atom of the ligand results in an improvement of the hydrolytic stability. The transfer of this concept to biphenylpropylsilanes by introducing two isobutyl groups therefore leads to a significant reduction of the hydrolysis and thus also of the interfering peak.

Fig. 1: Dissociation of biphenyl ligands

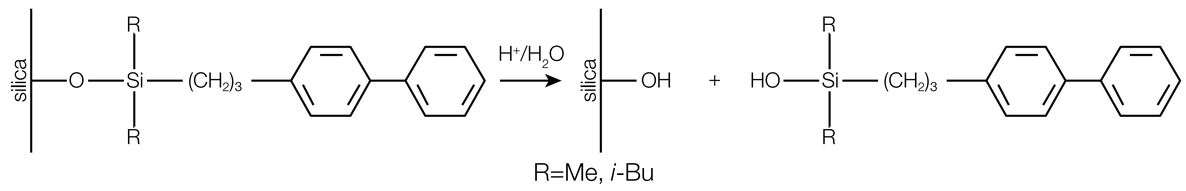
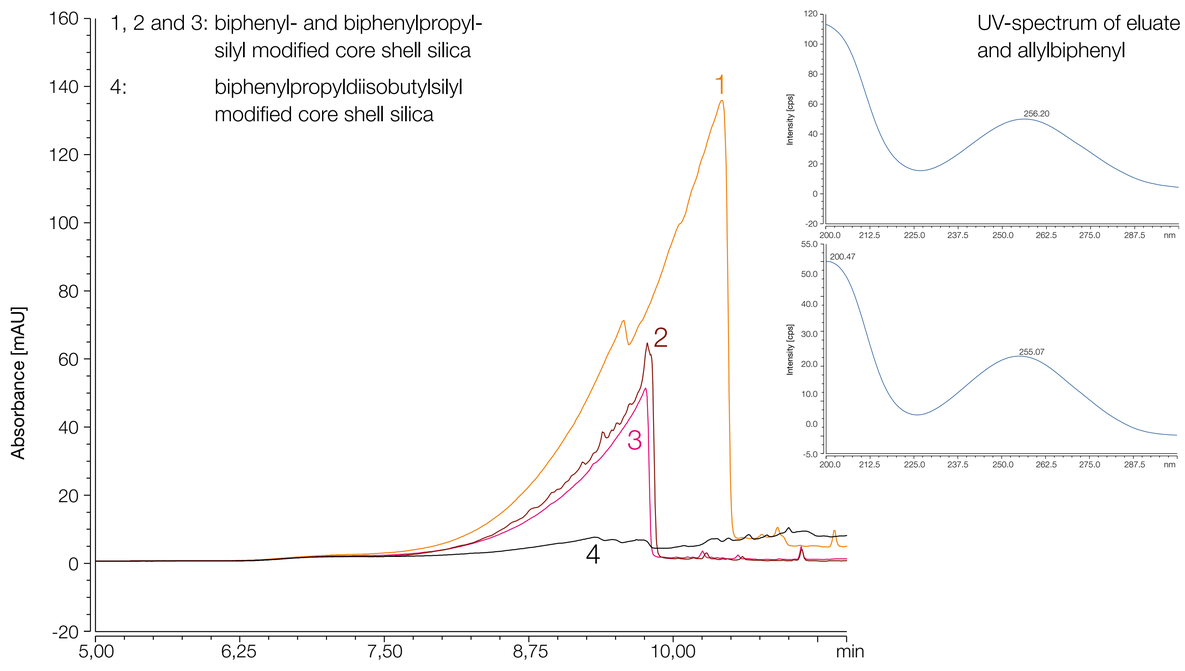


Fig. 2: Behavior of different biphenyl and biphenylpropyl stationary phases used with acidic gradients

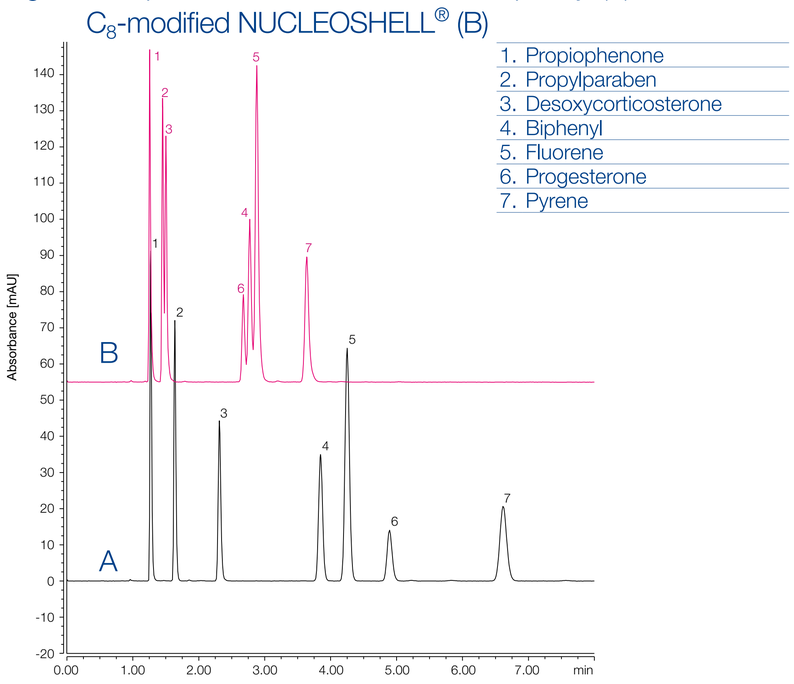


Chromatographic conditions:
Column: 100 mm x 3 mm
Eluent A: 1 % H_3PO_4
Eluent B: ACN
Temperature: 40 °C

Gradient: Equilibration 10 min 10 % B, hold 10 % B for 5 min, from 10 % to 90 % B in 5 min, hold 90 % B for 3 min, in 1.0 min to 10 % B, 0.56 mL/min
UV, 254 nm

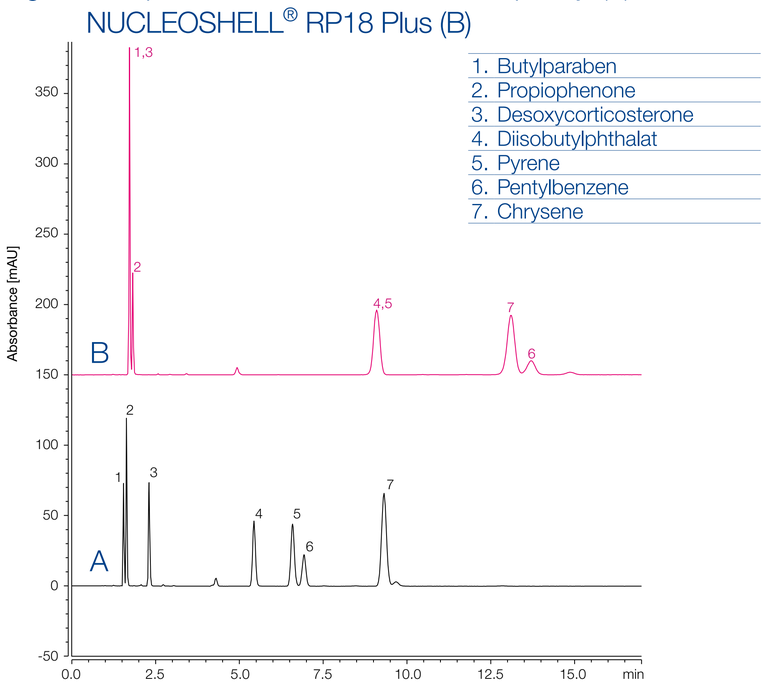
Selectivity of NUCLEOSHELL® Biphenyl and some NUCLEOSHELL® sorbents

Fig. 3: Comparison of NUCLEOSHELL® Biphenyl (A) and C_8-modified NUCLEOSHELL® (B)



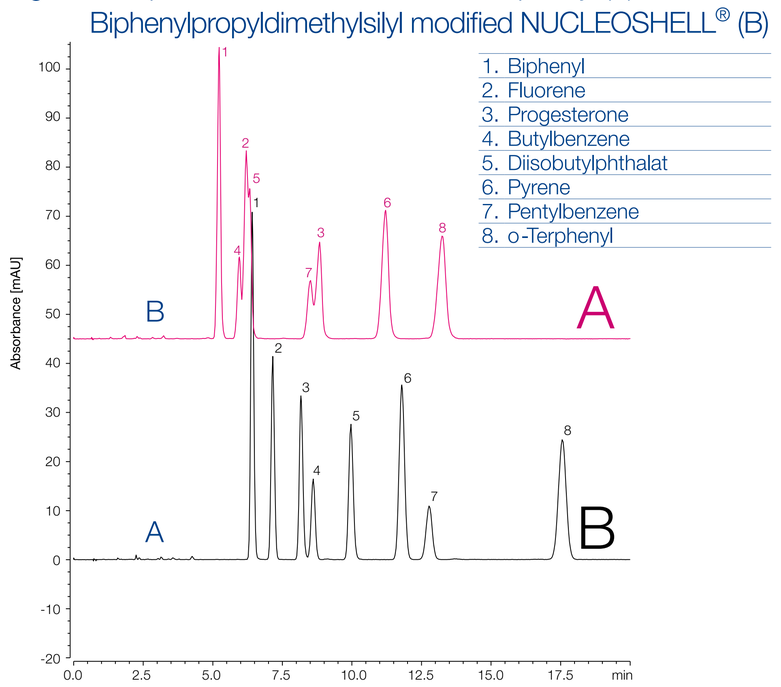
Chromatographic conditions:
100 mm x 3 mm, acetonitrile / water 55:45 (v/v), 0.56 mL/min, 40 °C
UV, 254 nm

Fig. 4: Comparison of NUCLEOSHELL® Biphenyl (A) and NUCLEOSHELL® RP18 Plus (B)



Chromatographic conditions:
100 mm x 3 mm, acetonitrile / water 55:45 (v/v), 0.56 mL/min, 40 °C
UV, 254 nm

Fig. 5: Comparison of NUCLEOSHELL® Biphenyl (A) and Biphenylpropyldimethylsilyl modified NUCLEOSHELL® (B)



Chromatographic conditions:
100 mm x 3 mm, acetonitrile / water 50:50 (v/v), 0.50 mL/min, 35 °C
UV, 254 nm

Conclusion

NUCLEOSHELL® Biphenyl 2.7 µm is a biphenylpropyldisobutylsilyl modified core shell silica. It shows a significant increase in hydrolytic stability compared to conventional biphenyl modifications under acidic conditions. As expected the different interactions of alkyl- and biphenyl-modified sorbents lead to selectivity differences (Fig 3 and 4). But also the two isobutyl groups affect the interactions clearly as the example in Fig. 5 shows. Nucleoshell biphenyl combines the advantages of a robust stationary phase with the interesting features of a biphenyl modification.

Literature:

[1] H. Riering, N. Bilmann, G. Cozzupoli 2016 Comparison of various aryl and alkyl modified Sorbents in RP chromatography, Poster ISC 2016, Cork (Online available *www.mn-net.com*/NUCLEODUR (Poster: Comparison of RP sorbents))

[2] J. J. Kirkland, J. L. Glajch, R. D. Farlee Anal. Chem. 61(1989) 2–11