

PHASE NEWS™

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Polar and Ionic Phases — Technique Tips

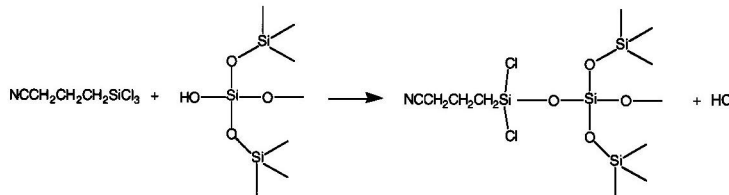
Of all the commonly employed bonded phases, polar and ionic phases provide the greatest challenge for reproducibility. These phases fall into three main classes:

Cyano Phases
Cationic Phases
Anionic Phases

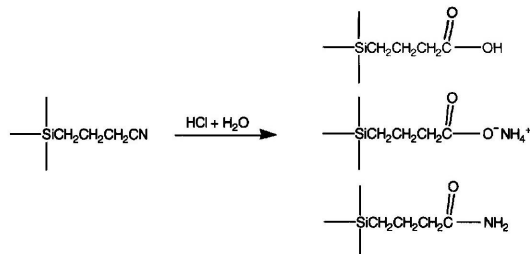
Each category has separate demands for achieving batch to batch consistency.

Cyano Phases

The most widely used cyano phases are derived from cyanopropylchlorosilanes, most usually cyanopropyltrichlorosilane or cyanopropyldimethylchlorosilane. The initial expectation is that the bonding proceeds through a simple displacement reaction.



Problems can occur due to the introduction of water to the reaction mixture. More often than not the water is deliberately introduced because it serves to polymerize the siloxane phase over the surface to increase the total amount of bonded phase. Water and hydrogen chloride react readily with the cyano group forming amides and carboxylic acids.



A random examination of bonded cyanophases used in both SPE and HPLC showed clear evidence of the presence of amides and carboxylates in over half of the samples tested. In two cases there was no evidence of the presence of cyano groups.

Action Points:

- 1.) If the bonded phase is working well in an established method, make sure your bonding method is reproducible. Put controls on the moisture content of the bonding solvent and support. Run FTIR DRIFT analysis to determine the nature of the bonded polar phase.
- 2.) If the bonded phase does not yield reproducible results, try the following: Put controls on the moisture content of the bonding solvent and support. During the bonding step apply a slow nitrogen sparge directly into the bonding reaction media; this removes HCl as it is formed.
- 3.) If a new phase is being created, methoxy or dimethylamino versions of the older chlorosilanes are frequently selected. These alternatives eliminate the formation of carboxylates. Methoxysilanes bond more slowly than the chlorosilanes. Dimethylaminosilanes react at rates similar to the chlorosilanes but are more costly.

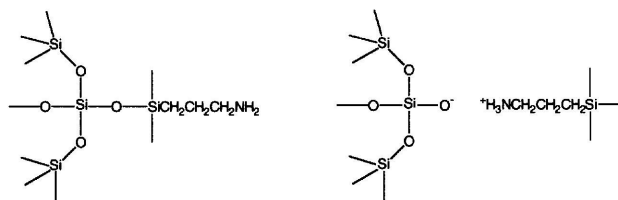
Other trends in cyanosilanes

Cyanopropylsilanes are ultimately prepared by a cyanide chemistry route. Environmental and safety considerations for these low volume chemicals is expected to result in significant price pressure. Cyanoethyl and cyanobutyl silanes, prepared by electrochemical synthesis, appear to be good alternatives.

Cationic Phases

Cationic phases are prepared either by direct bonding of quaternary amines or by post-bonding conversion of aminoalkylsilanes or chloroalkyl silanes. Direct bonding of quaternary silanes is usually reproducible. Post-bonding conversion allows greater latitude in creating unique bonded phases, but process control is more critical.

Cationic phases prepared by post-bonding conversion can suffer from poor stability due to the initial aminoalkylsilane bonding step. Frequently this is due to methods in which there is a hard acid pretreatment of the support. What occurs is an inverted, hydrolytically unstable, deposition of the silane.

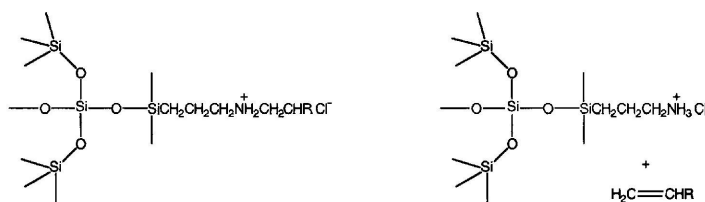


normal orientation - stable bond

inverted orientation - unstable

Proper orientation of aminosilanes is usually assured by deposition from aqueous alcohol, adjusting the water-alcohol-media pH within the range of 4.5-7.4 before silane introduction.

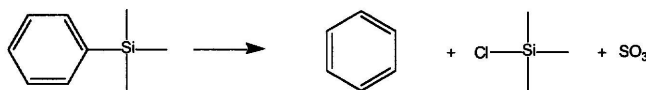
Cationic phases prepared by post-bonding conversion can exhibit variable retentions due to byproduct reactions during quaternization.



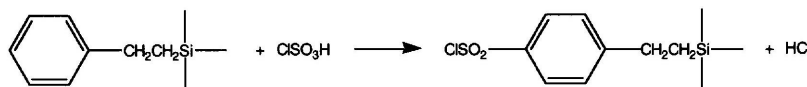
A balance has to be achieved between driving the quaternization reaction, which usually requires a minimum temperature of 80°, and the elimination reaction which becomes significant at temperatures >110° for quaternary chlorides.

Anionic Phases

The most common anionic phases are derived from the chlorosulfonation of aromatic silanes. Methods which involve the post-bonding conversion of phenyl groups suffer significant reproducibility problems if they are derived from phenyltrichlorosilane.



On the other hand, the reaction proceeds in relatively high yield if there is a spacer group between the electropositive silicon and the aromatic group.



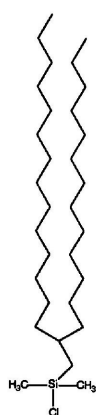
Direct bonding of cationic and anionic phases proceeds under typical bonding conditions in solvents ranging from methanol to toluene. There is a strong plus in reproducibility compared to post-bonding conversion. Only a limited number of silanes is available and customization is usually achieved by simultaneous bonding with C18 or other silanes.

Branched Silanes — A Progress Report

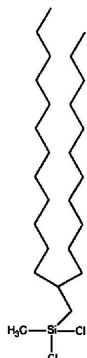
C23 Branched Silane Introduced

The drive to 100% aqueous media and higher bonding load for preparative separations has led to the introduction of tricocylmethyldichlorosilane. It shares the features of an asymmetric hydrophobic group and steric shielding depicted below.

Heptacocyl C27 Silane



Tricocyl C23 Silane



The increasing number of acidic analytes and the drive to aqueous media have generated a high level of interest in finding a way to create hydrophobic phases without the limitations of C18. Polar solvents are thought to induce phase (bed) collapse, a process which may be caused by self-association or crystallization of the long regular C18 chains.

Heptacocyl dimethylchlorosilane was introduced in 1999 as the first example of a new approach to generate more versatile hydrophobic phases for high pressure and preparative liquid chromatography. The C27 column has the advantage of longer

term retention stability of analytes compared to conventional C18 phases with straight aqueous mobile phases. The branched molecular structure of the C27 silane appears to minimize the phase collapse phenomenon. However, on extended exposure of the C27 phase to aqueous medium, a progressive, small loss of retention was observed. It was hypothesized that by reducing the chain length of the silane the phase collapse

phenomenon could be minimized or even eliminated. To test this hypothesis, a C23 silane, (tricocylmethyl)dimethylchlorosilane was prepared and bound to 5 micron silica. A separation of alkyl carboxylic acids on the C23 column is shown in Figure 2. In a 120 hour (5 day) experiment there was a 5% loss of retention, compared to a 50% loss of retention for the C27 column under the same conditions is shown in Figure 3. There was a total loss of retention with a C18 column in 15 hours. Unlike the C18 column, the C23 column retention can be regained with a 5 minute wash with methanol.

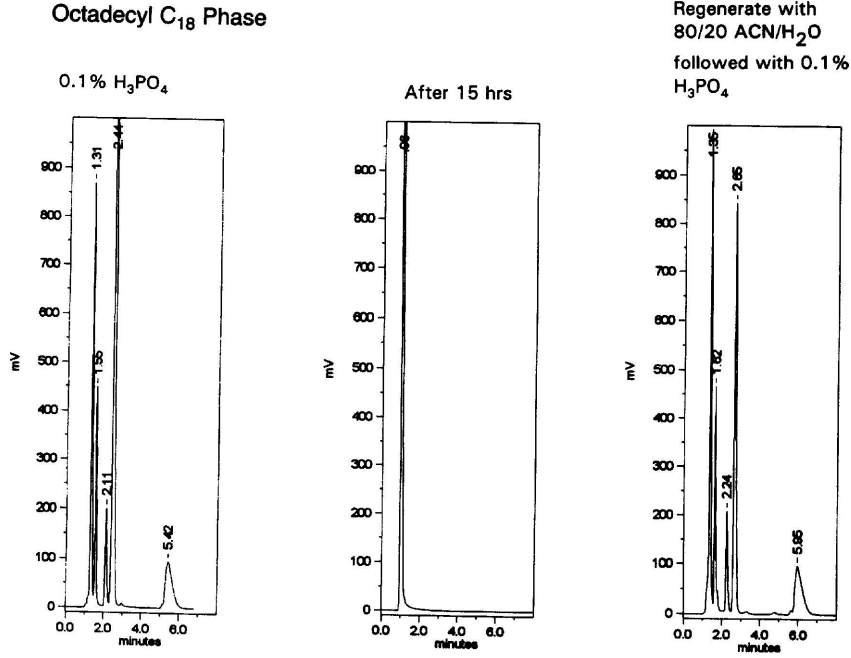


Figure 1

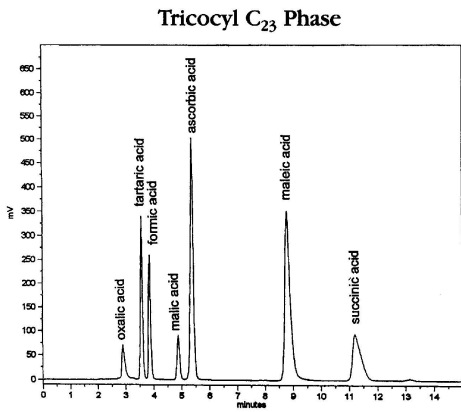


Fig. 2. Column-C23, 60-5, 250x4.66mm; Mobile Phase-0.1% H_3PO_4 , 1mL/min; Temperature 30°C; Detector-210 nm

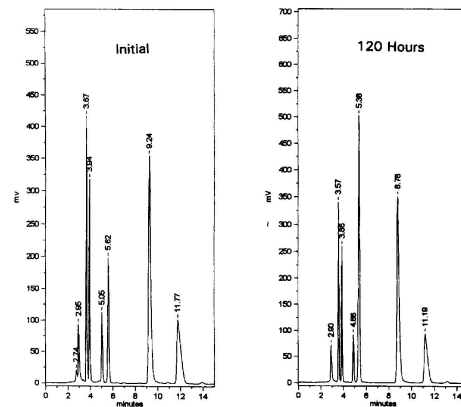


Fig. 3. Chromatograms - Alkyl Carboxylic Acids, Initial vs. 129 hours. Column - C23, 60-5, 250x4.6mm; Mobile Phase-0.1% H_3PO_4 , 1 mL/min; Temperature 30°C; Detector-210nm

SIC2266.0
1 3-(CHLORODIMETHYLSILYLMETHYL)HEPTACOSANE,
95%
10g/\$110.00

SIC2266.5
11-(CHLORODIMETHYLSILYLMETHYL)TRICOSANE
10g/\$95.00

PRODUCT SHORTS

Aldehyde Functional Silanes

The ability of aldehydes to form Schiff bases on reaction with amines leads to a variety of interesting applications for immobi-lization of biologically active molecules.

SIT8185.3
TRIETHOXSILYLBUTYRALDEHYDE, 90%
contains isomers 10g/\$60.00

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CYANOSILANES

SIC2437.0
 (3-CYANOBUTYL)METHYLDICHLOROSILANE
 [71550-62-4] TSCA HMIS: 3-2-1-X
 25g/\$40.00 100g/\$130.00

SIC2438.0
 (3-CYANOBUTYL)TRICHLOROSILANE
 [163155-56-4] HMIS: 3-2-1-X
 25g/\$39.00 100g/\$127.00

SIC2445.0
 2-CYANOENIYLTRIETHOXSILANE
 [919-31-3] TSCA HMIS: 2-2-0-X
 25g/\$15.00 100g/\$49.00

SIC2446.0
 2-CYANOETHYLTRIMETHOXSILANE
 [2526-62-7] HMIS: 3-2-1-X
 25g/\$40.00 100g/\$130.00

SIC2452.0
 3-CYANOPROPYLDIMETHYLCHLOROSILANE
 [18156-15-5] TSCA HMIS: 3-2-1-X
 25v/\$34.00 100k/\$110.00

SIC2453.0
 3-CYANOPROPYLMETHYLDICHLOROSILANE
 [1190-16-5] TSCA HMIS: 3-2-1-X
 25g/\$35.00 100g/\$114.00

SIC2453.5
 3-CYANOPROPYLMETHYLDIMETHOXSILANE
 HMIS: 3-2-1-X
 5.0g/\$27.00 25g/\$108.00

SIC2453.7
 3-CYANOPROPYLPHENYLDICHLOROSILANE
 [1078-96-2] TSCA HMIS: 3-2-1-X
 10g/\$94.00

SIC2454.0
 3-CYANOPROPYLTRICHLOROSILANE
 [1071-27-8] TSCA HMIS: 3-2-1-X
 25g/\$22.00 100g/\$72.00

SIC2455.0
 3-CYANOPROPYLTRIETHOXSILANE
 [1067-47-6] TSCA HMIS: 3-2-1-X
 25g/\$30.00 100g/\$94.00

SIC2456.0
 3-CYANOPROPYLTRIMETHOXSILANE
 [55453-24-2] TSCA-L HMIS: 3-2-1-X
 10g/\$30.00 50g/\$140.00

SIC2456.5
 11-CYANOUNDECYLTRIMETHOXSILANE
 HMIS: 2-1-0-X
 5.0g/\$146.00

CATIONIC SILANES

SID3392.0
 N,N-DIDECYL-N-METHYL-N-(3-TRIMETHOXY-
 SILYLPROPYL)-AMMONIUM CHLORIDE, 42% in
 methanol
 [68959-20-6] TSCA HMIS: 3-4-0-X 25g/\$46.00

SIO6620.0
 OCTADECYLDIMETHYL(3-TRIMETHOXY-
 SILYLPROPYL)-AMMONIUM CHLORIDE, 60% in
 methanol
 [27668-52-6] TSCA HMIS: 3-4-0-X
 25g/\$24.00 2kg/\$280.00

SIT8395.0
 N-(TRIMETHOXSILYLETHYL)BENZYL-N,N,N,-
 TRIMETHYLAMMONIUM CHLORIDE, 60% in
 methanol
 HMIS: 3-3-1-X 25g/\$80.00

SIT8415.0
 N-TRIMETHOXSILYLPROPYL-N,N,N-
 TRIMETHYL-
 AMMONIUM CHLORIDE (50% in methanol)
 [35141-36-7] TSCA HMIS: 2-4-1-X
 5g/\$17.00 400g/\$210.00

ANIONIC SILANES

SIC2415.0
 2-(4-CHLOROSULFONYLPHENYL)ETHYL-
 TRICHLOROSILANE,
 50% in methylene chloride
 [79793-00-3] TSCA HMIS: 4-2-2-X
 25g/\$45.00 100g/\$148.00

SIC2415.4
 2-(4-CHLOROSULFONYLPHENYL)ETHYL-
 TRICHLOROSILANE, 50% in toluene
 [79793-00-3] TSCA HMIS: 4-4-2-X
 25g/\$49.00 100g/\$159.00

SIC2417.0
 2-(4-CHLOROSULFONYLPHENYL)ETHYL-
 TRIMETHOXSILANE, 50% in methylene
 chloride
 HMIS: 3-2-1-X
 25g/\$68.00 100g/\$221.00

SIT8378.3
 3-(TRIHYDROXSILYL)-1-PROPANE-
 SULFONIC ACID, 45-50% in water
 [70942-24-4] TSCA HMIS: 3-0-0-X
 25g/\$48.00