Investigation of C_{18} Bonding Chemistry on Novel Hybrid Organic/Inorganic Particles

John E. O'Gara, Daniel P. Walsh, Alan R. Pelissey, Bonnie A. Alden, Christina A. Gendreau, Pamela C. Iraneta, and Thomas H. Walter

Waters Corporation, 34 Maple Street, Milford, MA 01757-3696 USA

Summary:

A novel hybrid organic/inorganic particle is compared to a classical high purity silica with respect to C_{18} silane bonding chemistry. Monofunctional, trifunctional, and embedded polar group C_{18} silanes were bonded onto both materials under similar reaction conditions. Bonded phase data are presented that characterize the differences and similarities between the two substrates. In addition, chromatographic data are presented for each bonded phase, where capacity factor and peak shape were measured using a set of neutral, polar, and basic test analytes.

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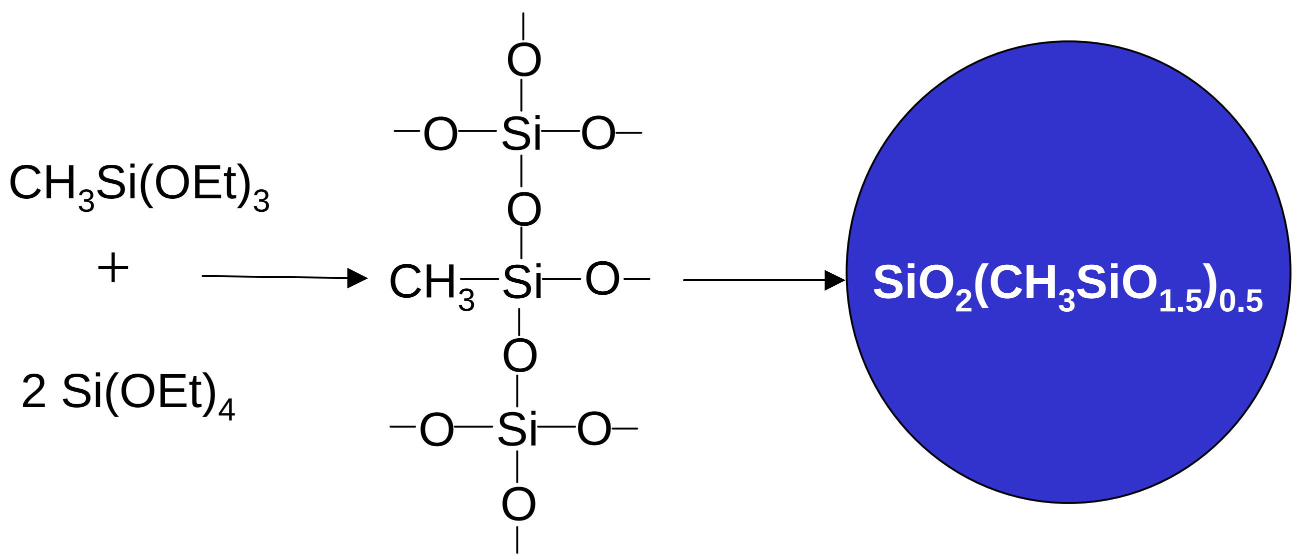
Hybrid Organic/Inorganic Particle Technology

•Hybrid Organic/Inorganic materials contain both organic and inorganic components

•The hybrid particles described here were synthesized from $Si(OEt)_4$ and $CH_3Si(OEt)_3$:



• Hybrid particles combine:
  - •efficiency and mechanical strength of silica
  - •extended pH range and absence of base tailing of organic polymers

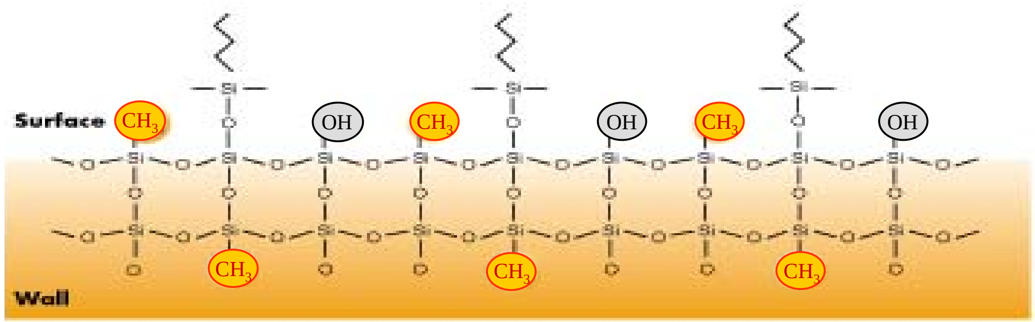
Characteristics & Surface Structure: Hybrid vs. Silica Supports

•Characteristics of Silica and Hybrid Supports:

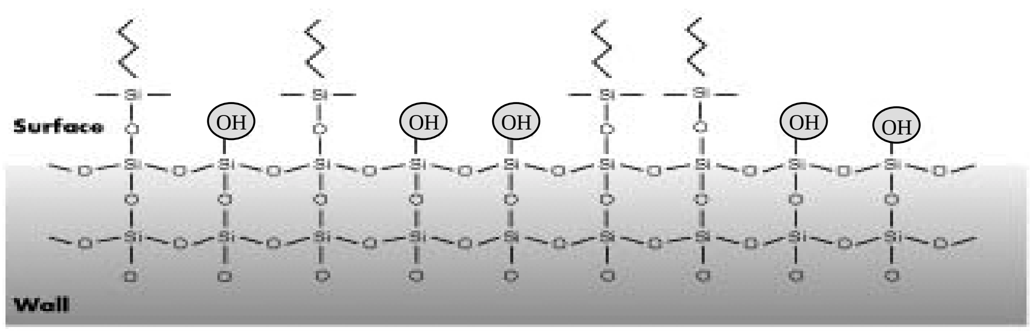
	Hybrid*	Silica
Avg. Particle Diameter, µm	5.0	5.0
Specific Surface Area, m^2/g	173, 174	325
Pore Volume, cm^3/g	0.72, 0.69	0.84
Avg. Pore Diameter, Å	145, 140	92
Carbon Content, % w/w	6.9, 6.6	0.0
Aluminum Content, ppm w/w	2, 1	0
Iron Content, ppm w/w	8, 3	4
Sodium Content, ppm w/w	4, 1	0

* Two Hybrid Lots Used. Second entry used for Embedded Carbamate Bonding.

•Surface Structure of Silica and Hybrid Supports:



Bonded XTerra™ Particle



Bonded Silica Particle

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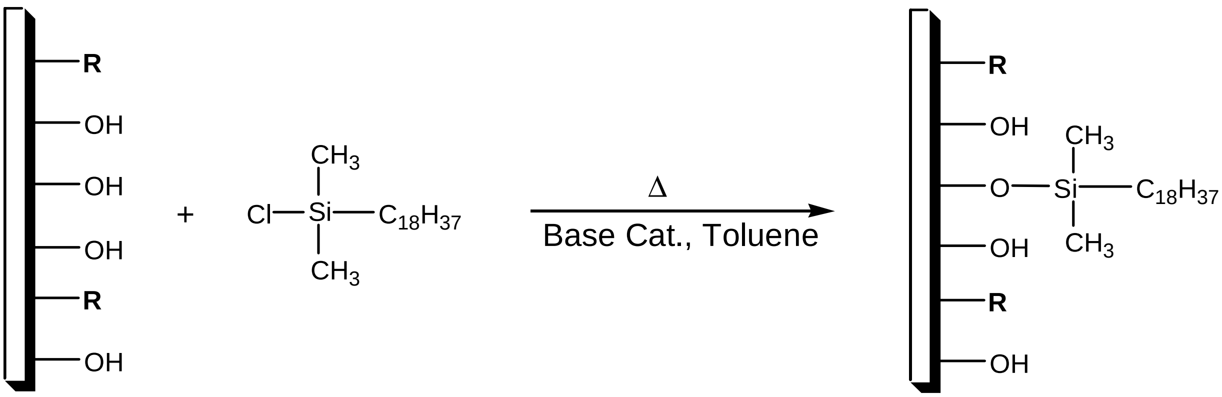
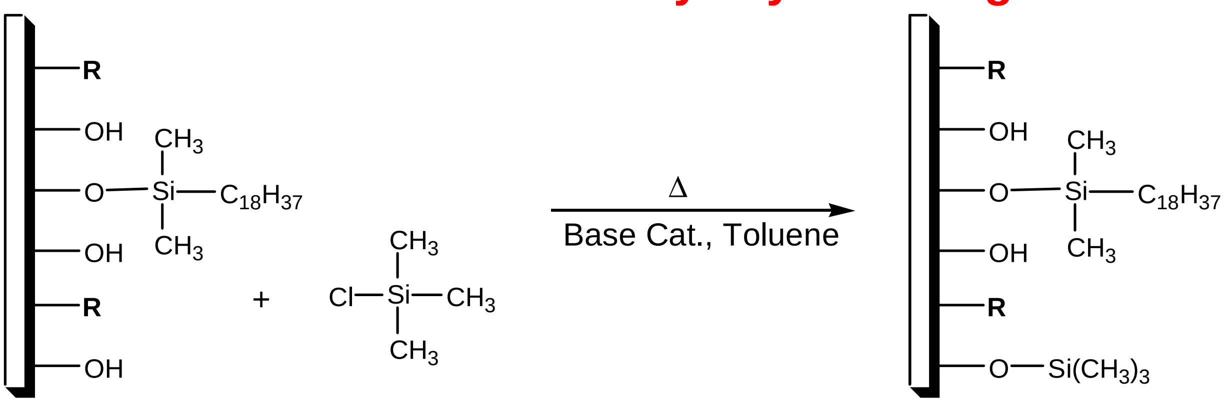
Monofunctional C_{18} Phase Data

Surface Reaction #1: C_{18} Bonding



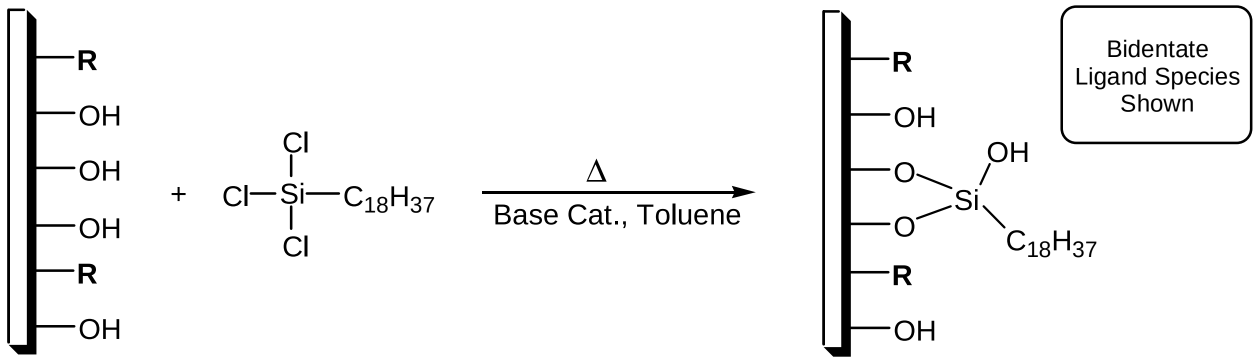
Surface Reaction #2: Trimethylsilyl Bonding



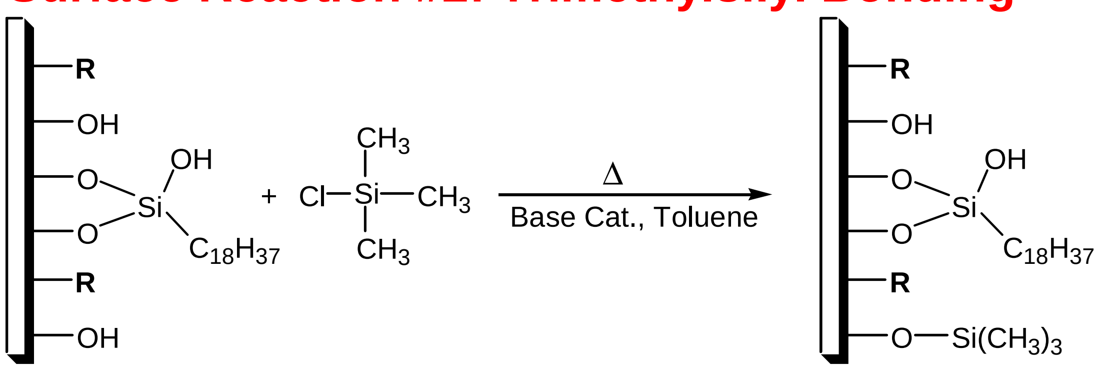
%C From:	Hybrid Phase $R = CH_3$	Silica Phase R = OH
Base Particle	6.9	0.0
C_{18} Ligand	8.0	19.2
TMS Ligand	0.3	0.3
Total %C	15.2	19.5
C_{18} Surface Conc.µmol/m^2)	2.16	3.19

Trifunctional C_{18} Phase Data

Surface Reaction #1: C_{18} Bonding



Surface Reaction #2: Trimethylsilyl Bonding



%C From:	Hybrid Phase $R = CH_3$	Silica Phase $R = OH$
Base Particle	6.9	0.0
C_{18} Ligand	8.0	18.4
TMS Ligand	0.8	0.8
Total %C	15.7	19.2
C_{18} Surface Conc.$\mu mol/m^2$)	2.42	3.51

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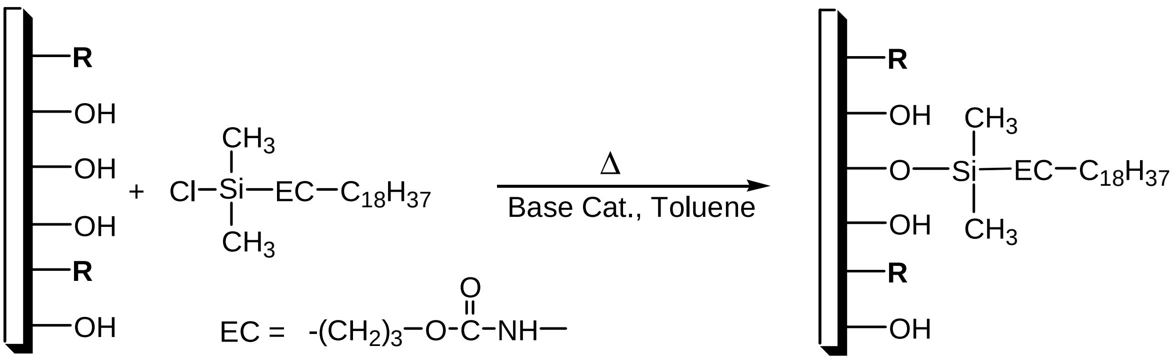
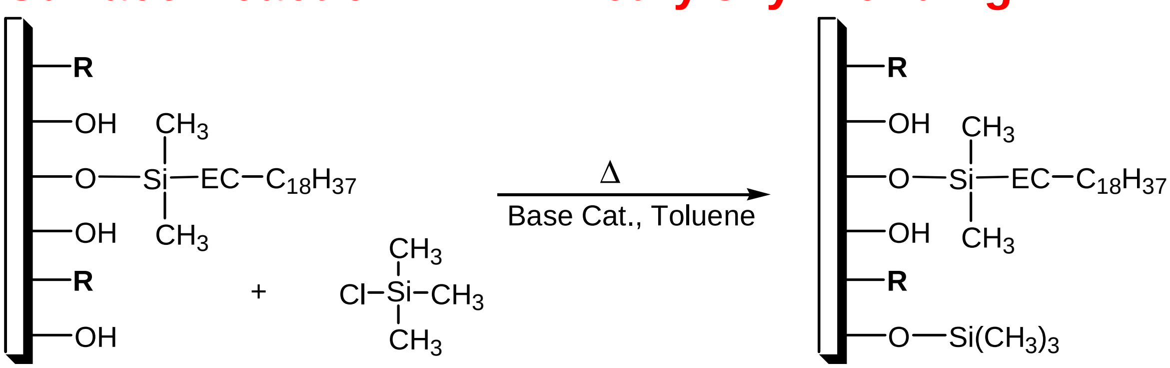
Embedded Carbamate C_{18} Phase Data

Surface Reaction #1: Embedded Carbamate C_{18} Bonding

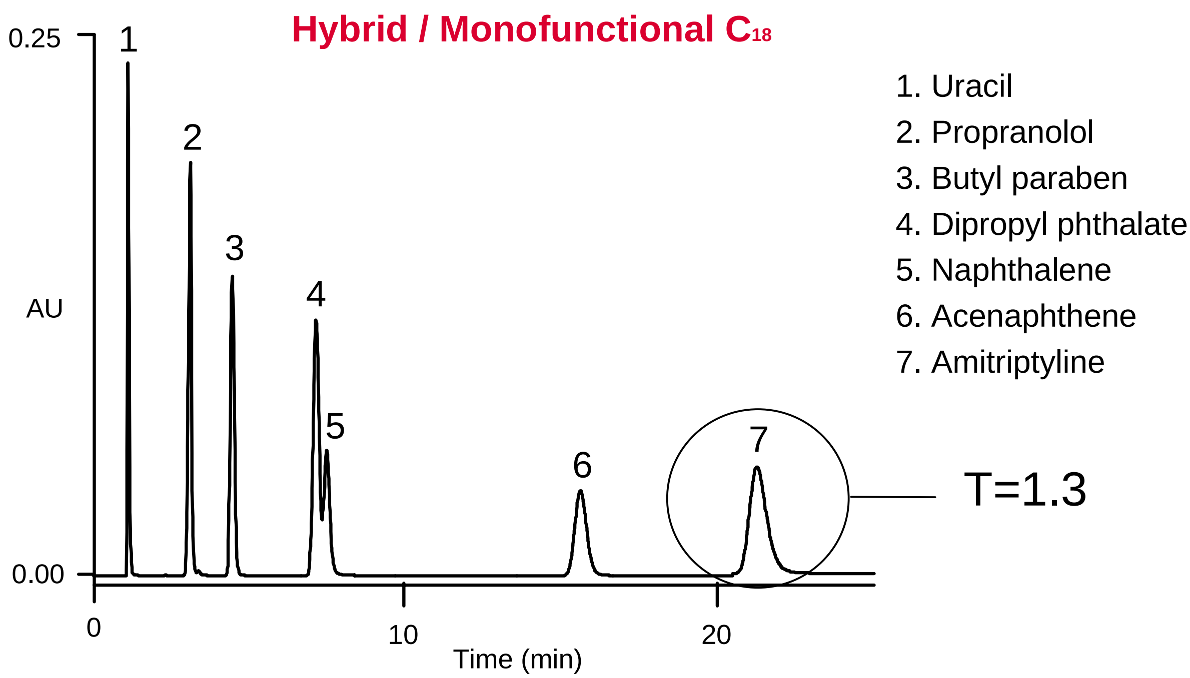


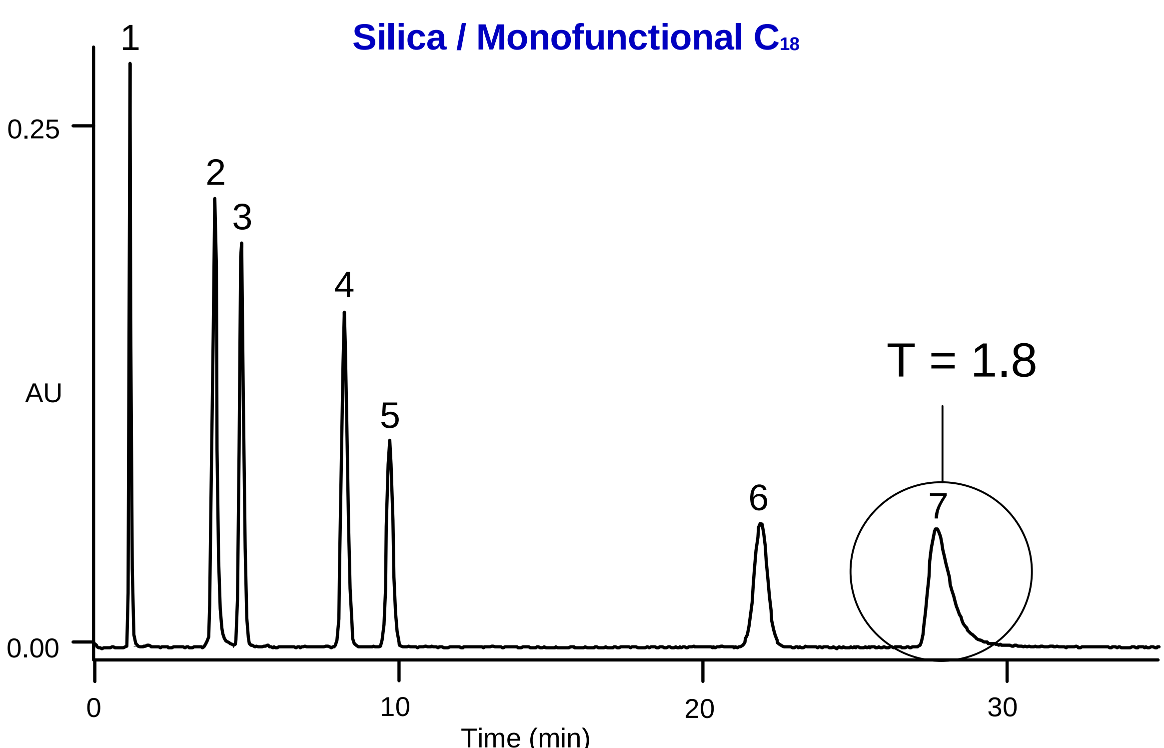
Surface Reaction #2: Trimethylsilyl Bonding



%C From:	Hybrid Phase $R = CH_3$	Silica Phase $R = OH$
Base Particle	6.6	0.0
C_{18} Ligand	8.1	21.2
TMS Ligand	0.1	0.3
Total %C	14.8	21.5
C_{18} Surface Conc.µmol/m^2)	1.81	3.14

Monofunctional C_{18} Chromatograms





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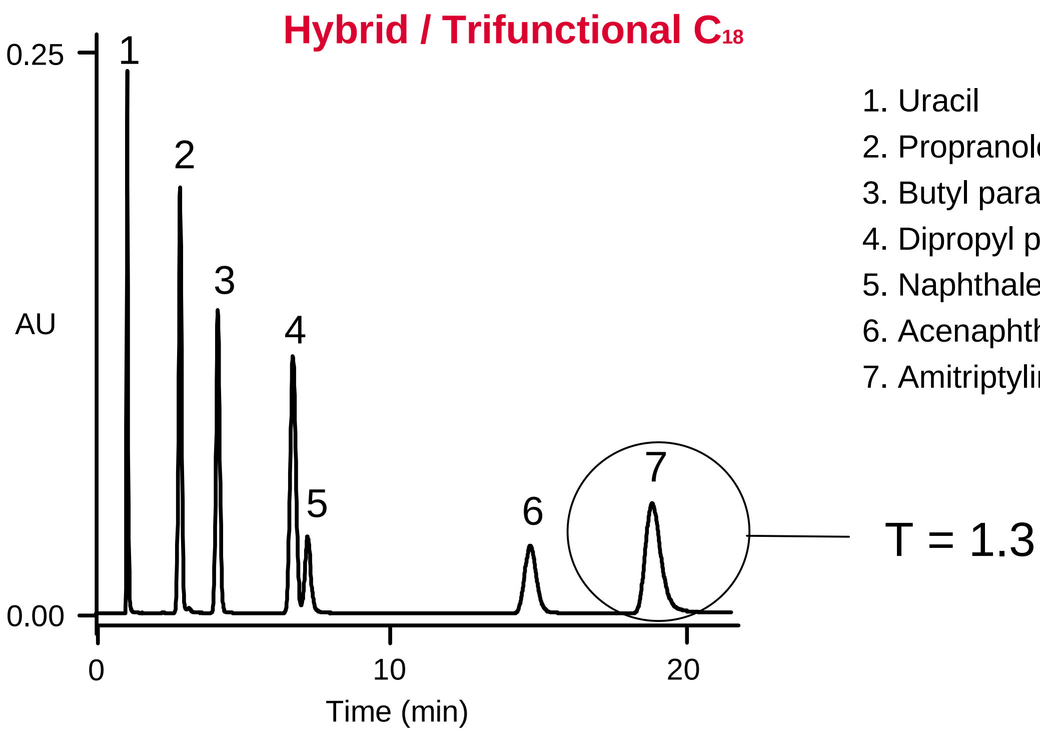
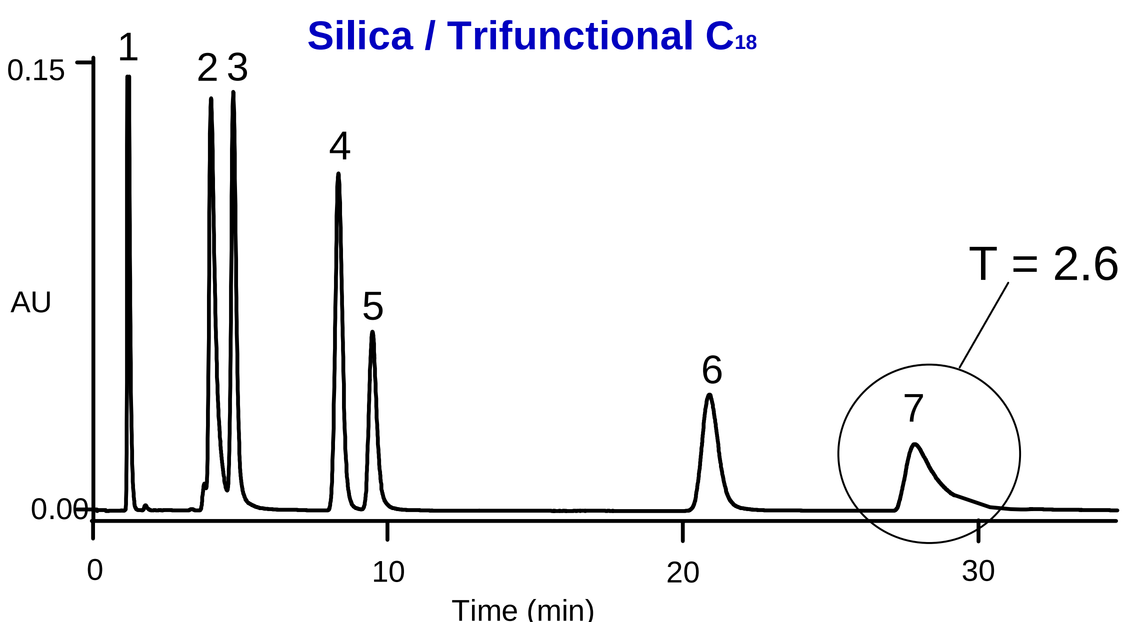
Trifunctional C_{18} Chromatograms



1. Uracil
2. Propranolol
3. Butyl paraben
4. Dipropyl phthalate
5. Naphthalene
6. Acenaphthene
7. Amitriptyline



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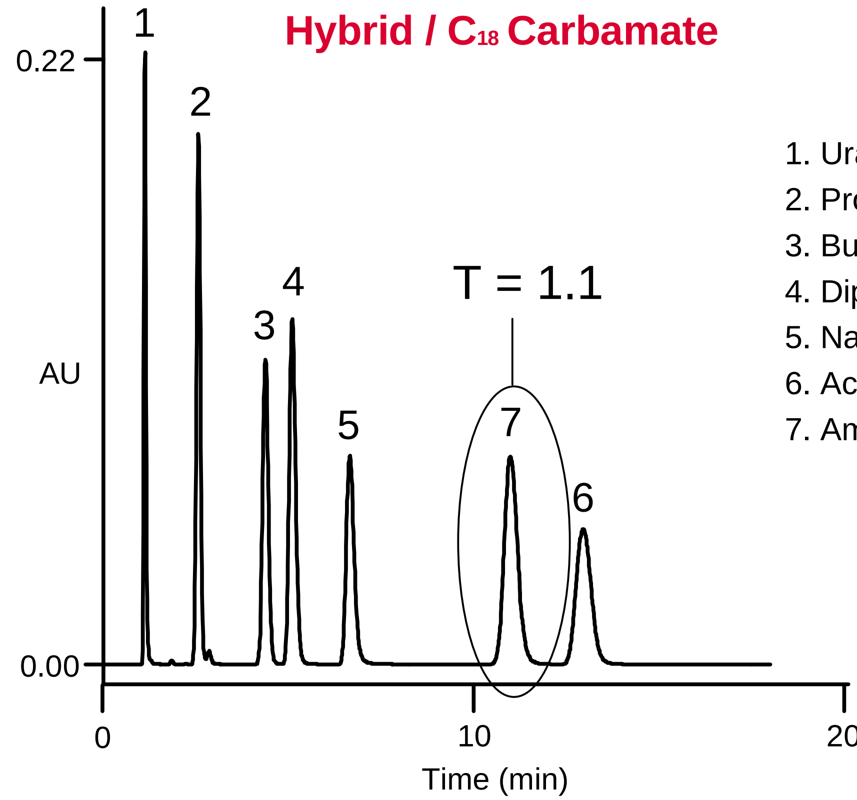
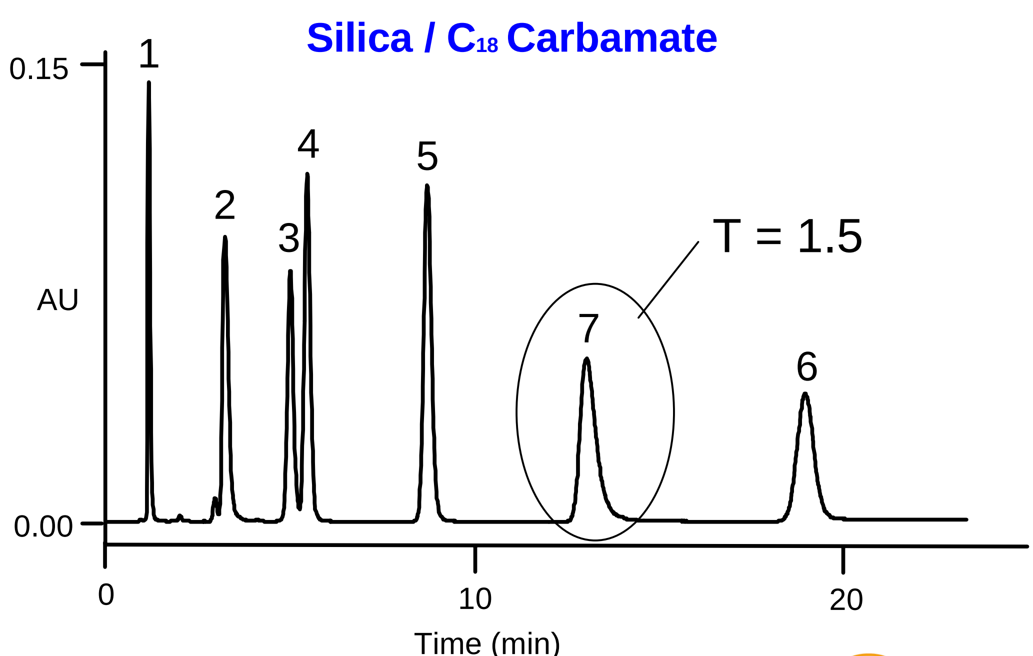
Embedded Carbamate C_{18} Chromatograms



1. Uracil
2. Propranolol
3. Butyl paraben
4. Dipropyl phthalate
5. Naphthalene
6. Acenaphthene
7. Amitriptyline



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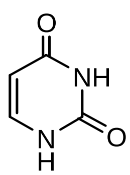
Chromatographic Testing

Conditions

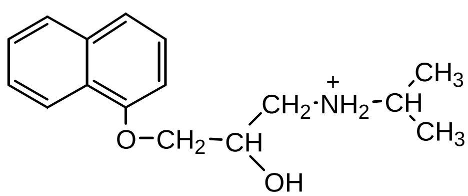
- 65:35 MeOH/20 mM KH_2PO_4/K_2HPO_4, pH 7.00
- Flow Rate: 1.0 mL/min
- Temperature: 23.4 ± 0.1 ºC

Analytes

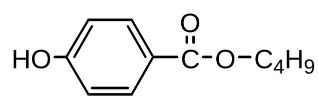
1) Uracil



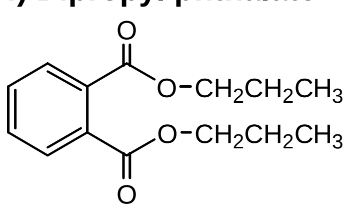
2) Propranolol, pK_a = 9.6



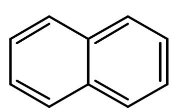
3) Butyl paraben



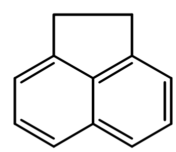
4) Dipropyl phthalate



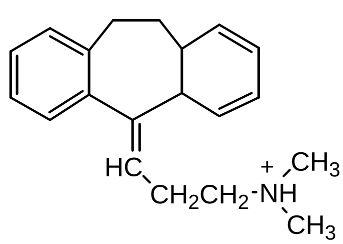
5) Naphthalene



6) Acenaphthene



7) Amitriptyline, pK_a = 9.4



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Chromatographic Data

Ligand & Analyte	Hybrid Phase $R = CH_3$	Silica Phase $R = OH$
Monofunctional C_{18}	*Retention Factor k (USP Tailing)*	
1. Uracil	-----	-----
2. Propranolol	1.64 (0.8)	2.01 (1.6)
3. Butyl paraben	2.74	2.67
4. Dipropyl phthalate	4.94	5.25
5. Naphthalene	5.22	6.37
6. Acenaphthene	11.90 (1.1)	15.64 (1.0)
7. Amitriptyline	16.54 (1.3)	20.02 (1.8)
Trifunctional C_{18}		
1. Uracil	-----	-----
2. Propranolol	1.55 (0.9)	2.28
3. Butyl Paraben	2.63	2.90
4. Dipropyl phthalate	4.81	5.79
5. Naphthalene	5.24	6.72
6. Acenaphthene	11.70 (1.1)	15.99 (1.3)
7. Amitriptyline	15.23 (1.3)	21.56 (2.6)
Embedded Carbamate C_{18}		
1. Uracil	-----	-----
2. Propranolol	1.17 (1.0)	1.78 (1.6)
3. Butyl Paraben	2.63	3.27
4. Dipropyl phthalate	3.22	3.67
5. Naphthalene	4.47	6.45
6. Acenaphthene	9.56 (1.1)	15.19 (1.1)
7. Amitriptyline	7.97 (1.1)	10.21 (1.5)

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Conclusions

Hybrid vs. Silica Based C_{18} Bonded Phases

• For all three ligands lower C_{18} surface concentrations were obtained on the Hybrid particles due to their reduced surface silanol concentration

• Hybrid C_{18} Phases showed reduced analyte retentions on all three phases due to the lower surface area of the particle and the lower C_{18} surface concentrations

• Hybrid C_{18} Phases showed similar efficiency and selectivity as the corresponding Silica phases

• Hybrid C_{18} Phases showed reduced tailing factors for basic analytes, due to their reduced surface silanol concentration

Note:

XTerra™ packings based on Hybrid Particle Technology are now available from Waters Corporation