supelco HPLC and GC columns and accessories

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Leading Innovations in HPLC

Stable 5 µm (2 nd after DuPont)	
Monomeric bonded phase (maybe 1 st)	ate
5 cm columns for fast analysis (1 st)	970s
Base-deactivated (1 st) (DB)	1
3 µm porous silica (2 nd after Perkin-Elmer)	
Special applications:	
 Specialty column for tricyclic antidepressants (1st) (LC-PCN) 	
 15 cm column for fast analysis of PAHs (1st, maybe 2nd after P-E) (LC-PAH) 	
 Nucleoside and nucleotide columns (1st) (LC-18-S, LC-18-T) 	
 Direct serum injection phase (2nd after Pinkerton) (Hisep SHP) 	
 Chiral phases (Many 1^{sts}) (Astec) 	
Polar embedded (1 st) (amide-based phases, Suplex, ABZ, RP-Amides)	¥
Fused-Core technology (co-1 st with AMT) (Ascentis Express) To	oday
Titan – UHPLC columns with Monodisperse Silica	,



Supelco HPLC Product History

2013: Titan

2007: Ascentis Express

1998: Chirobiotic (by Astec)

Mid-1990s: Ascentis

1990s: Discovery

1970s: Supelcosil

Extensive knowledge and understanding of bonding chemistry by the R&D team of Supelco drove the innovations.

1978

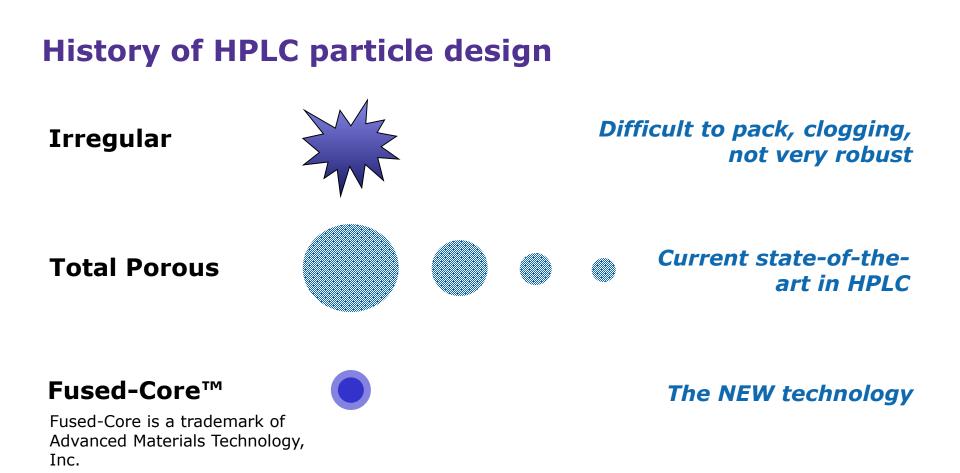






Ascentis Express – Fused-Core Technology

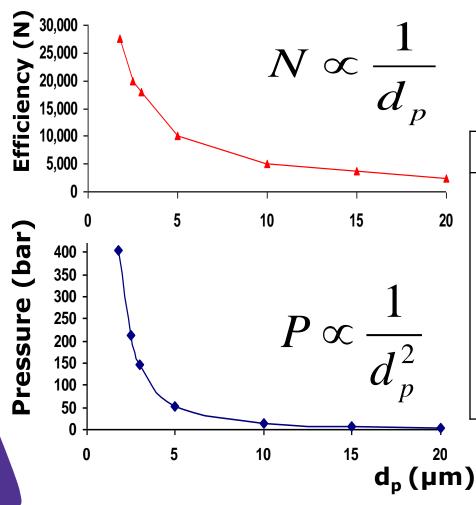
www.sigmaaldrich.com/express



Nowadays also known as core-shell, superficially porous, solid-sore, ...

6

Particle size: Influence on efficiency and pressure

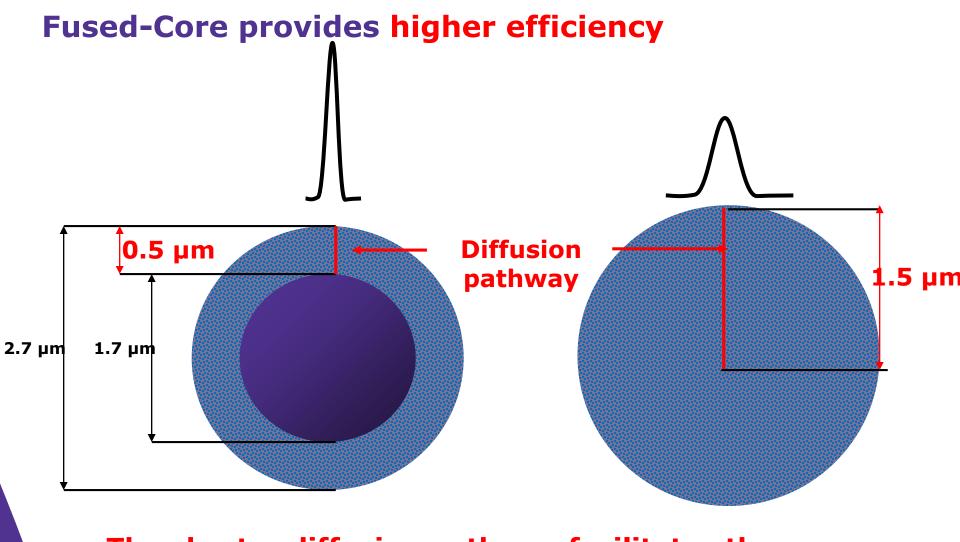


Doubling the efficiency by halving the particle size results in a pressure increase by a factor of four.

Particle (µm)	psi	bar	Ν
1.8	5889	406	27,500
2.5	3089	213	20,000
3	2118	146	16,500
5	769	53	10,000
10	189	13	5,000
15	87	6	3,750
20	44	3	2,500

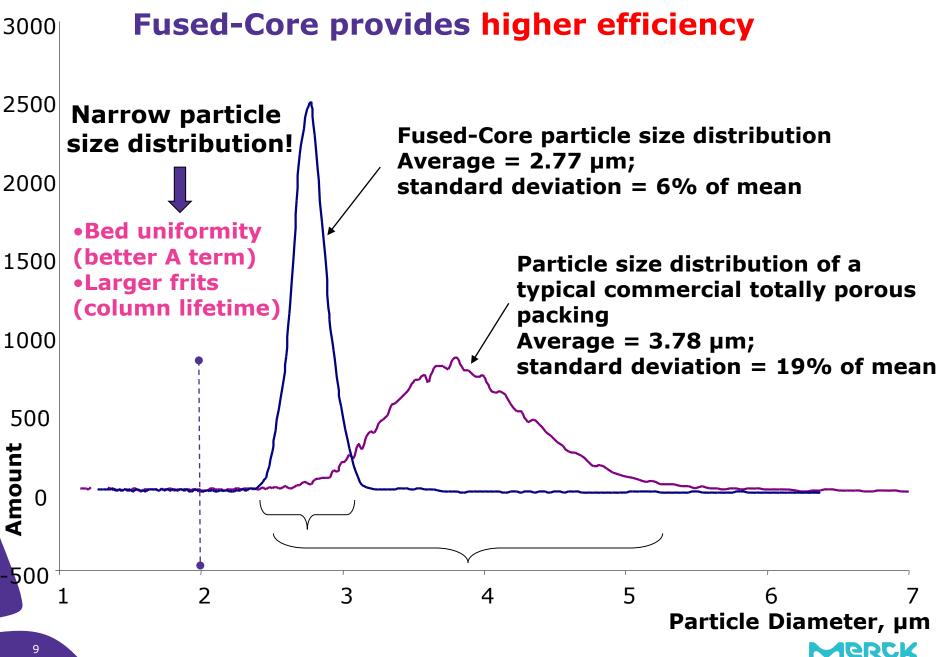
10 cm column, 3 mm/s linear velocity



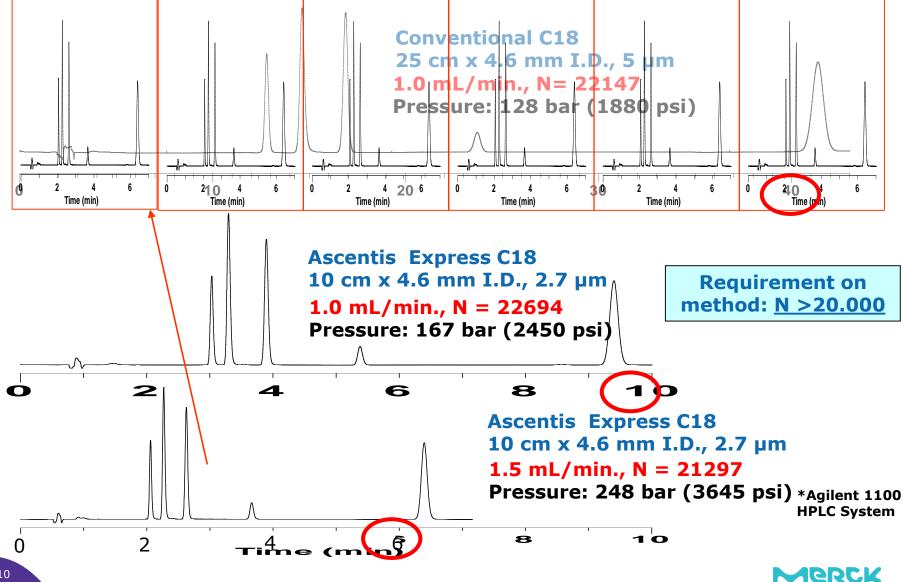


The shorter diffusion pathway facilitates the mass transfer (C term)!

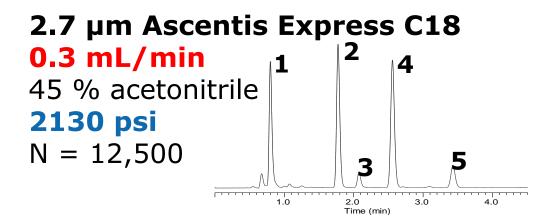


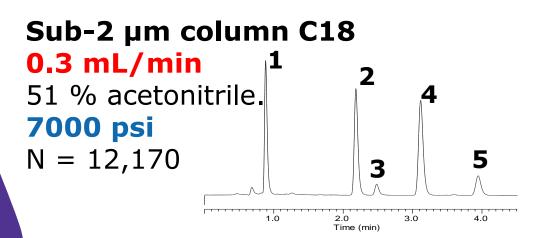


Increasing speed on traditional HPLC systems*



Same efficiency compared to sub 2µm particles





Mobile Phase:

water : acetonitrile; isoelutropic for β -Estradiol

Columns: 100 x 2.1 mm

- Flow: 0,3 mL/min
- Det: 200 nm

Inj: 1µL

Elution order:

- 1. Estriol
- **2.** β -Estradiol
- 3. Contaminant
- 4. Estrone
- 5. Estrone
- degradant



Fused-Core Milestones - Pioneering the Particles

2007: First 2.7 µm FC particles to achieve efficiencies >250,000 N/m

- Efficiencies comparable to sub-2 µm particles
- Pressure drop (flow resistance) comparable to 3 μm particle columns

2012: 5 µm FC particles to achieve efficiencies >150,000 N/m

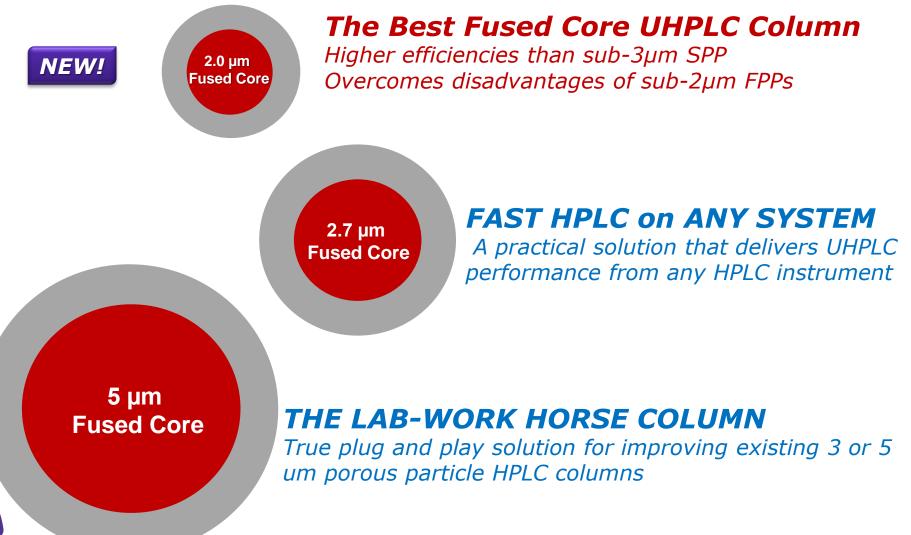
- Operate at low pressures with unsurpassed ruggedness.
- Efficiencies exceed most 3 µm particles (150,000 N/m observed routinely at low pressure)
- Pressure drop of 5 µm particle columns
- Designed for traditional instruments & routine methods.

2014: 2.0 µm FC particles for superior performance in UHPLC

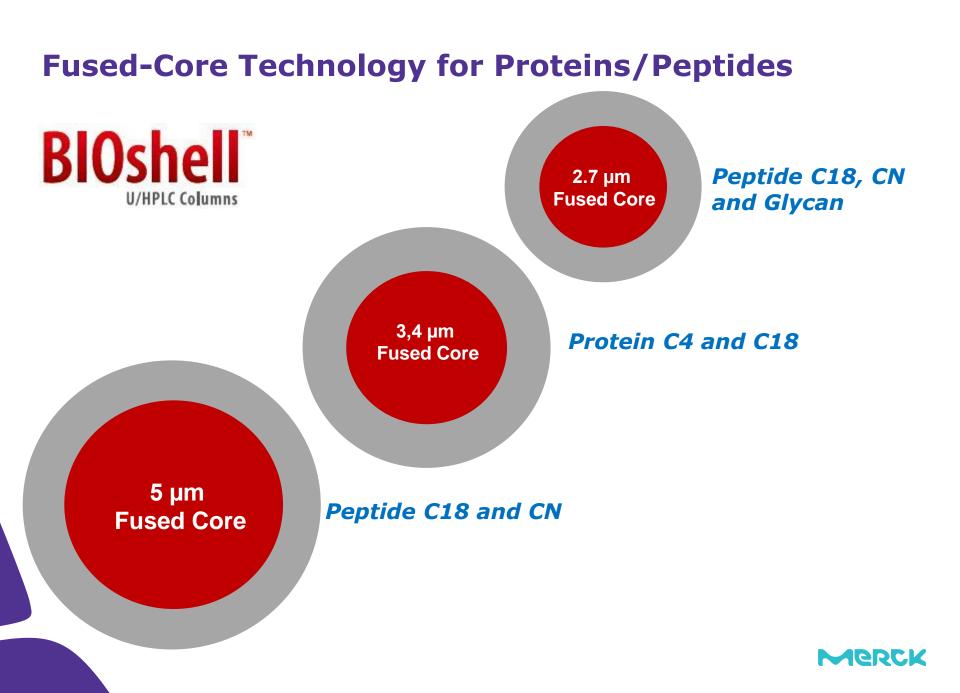
- Outperforms fully porous sub-2 µm particles in efficiency
- Perfect balance of pressure and performance
- Based on Fused-Core particle design geared toward maximizing performance of UHPLC systems



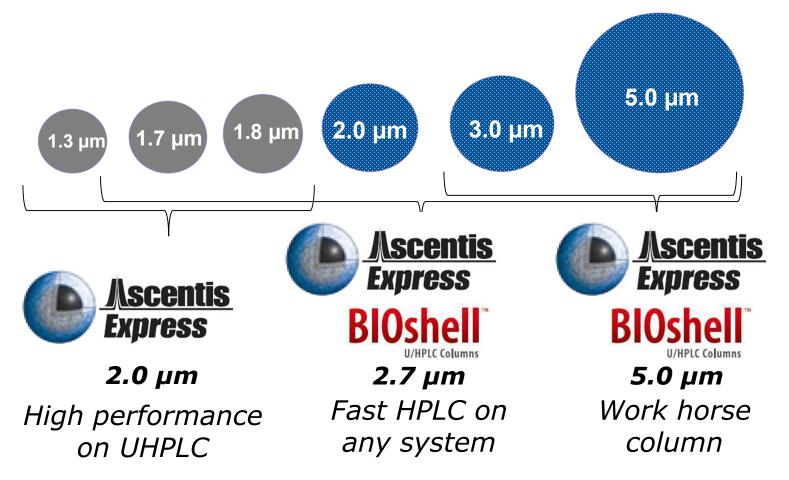
Ascentis Express Fused-Core Particles







Which particle size for which approach? UHPLC HPLC



Ascentis Express Fused-Core HPLC Phases

5.0µm	2.7 µm	2.0 µm	Phase type
C18	C18	C18	Non-polar (RP)
C8	C8	C8	Non-polar (RP)
	Biphenyl		Non-polar (RP)
Phenyl-Hexyl	Phenyl-Hexyl	Phenyl-Hexyl	Non-polar (RP)
RP-Amide	RP-Amide	RP-Amide	Medium/high polarity
F5	F5	F5	Medium/high polarity
ES-Cyano	ES-Cyano	ES-Cyano	Medium/high polarity
ОН5	OH5	OH5	HILIC
HILIC (silica)	HILIC (silica)	HILIC (silica)	HILIC

Broadest offering of stationary phases on Fused-core (and all core-shell) particles!





Supelco GC Product History

- 1983 SP-2560: 1. Special Column (FAMEs)
- 1984 SPB-608: 1. Special Column (Pesticide/PCBs)
- 1984 SUPELCOWAX 10: 1. Column with bonded Wax
- 1985 SP-2331: 1. Special Column (Dioxins)
- 1986 VOCOL: 1. Special Column (VOCs)
- 1987 Sup-Herb: 1. Special Column (Herbicides)
- 1988 Petrocol DH: 1. Spec. Column (100 m, Petrochem.)
- 1989 Petrocol DH 150: 1. Column with 150 m
- 1989 Petrocol 2887: 1. Special Column (ASTM D2887)
- 1990 Omegawax: 1. Special Column (omega FAMEs)
- 1991 SPB-1 SULFUR: 1. Special Column (Sulfur comp.)
- 1993 SAC-5: 1. Special Column (free sterols)
- 1994 Carboxen-1006 PLOT: 1. Carboxen PLOT Column
- 2008 SLB-IL100: 1. Column with ionic liquids
- 2010 SLB-IL111: 1. Column with highest polarity

THIN LAYER CHROMATOGRAPHY COLUMN CHROMATOGRAPHY HIGH - PURITY LIPIDS AND SUPPLIES

GAS CHROMATOGRAPHY

FALL 1967

The us introduce you to our complete kine of materials for the richas of easy chromatography, thin layer dromatography and high-purity, tipid research, the ore offering a generous section on marked and impacked columns. There are also various supports, and several new products, never secore offering a generous section of the support of an one offer higgs, supports on the market. If it hanness that you don't see what you need, please feel free to call us. Suppler on the market. If it hanness that you don't see what you need, please feel free to call us. Suppler on the market of the how how working for you... make we of it.





Supelcos Offering GC Columns – Product Lines

- Over 80 different column chemistries (non-chiral and chiral)
- Each with a different combination of retention mechanisms (selectivity)
- Can serve many industries and applications
- <u>Strengths</u>
 - Highly polar columns
 - Application-specific columns

- Supelcos Ionic Liquid GC columns represent a new column platform
- Benefits
 - Unique selectivity
 - Better phase stability



Visit sigma-aldrich.com/gc-columns for more information.

sigma-aldrich.com/gc



Highlight GC Columns by Supelco

SLB-5ms

• General use, very low bleed column, bur at a very competitive price

SP-2331

• SP-2331 is one of the benchmark columns for dioxin analysis

SPB-Octyl

• SPB-Octyl is one of the few columns that can separate most PCB congeners

Petrocol DH series

- Benchmark columns for this application
- Many retention index libraries are based on these columns

PLOT columns

- Supelco offers some of the best PLOT columns in the world
- In particular, the Carboxen-1010 PLOT (only column to separate oxygen, nitrogen, and carbon dioxide)



Highlight GC Columns by Supelco

SP-2560

- SP-2560 is the benchmark column for the separation of cis/trans FAME isomers
 SUPELCOWAX 10
- Highest maximum temperature (280 °C) of any PEG phase column

Omegawax

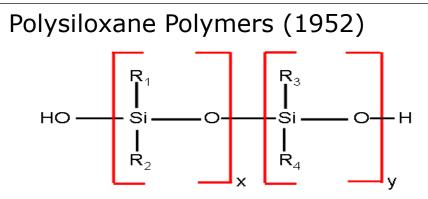
 Omegawax is the benchmark column for the separation of omega 3 and omega 6 FAMEs

Astec CHIRALDEX, Supelco DEX

- For separation of enantiomers
- 25 unique specialized phases that incorporate derivatized cyclodextrins
 - Broad range of selectivities
 - Likely we offer a column to perform any enantiomeric GC separation



Overview Example Structures of Non-Ionic Liquid Phases



Drawbacks

- Active hydroxyl (-OH) groups at polymer termini allow a back-biting reaction
 - Results in phase degradation
 - Contributes to column bleed
- Chemistry modifications are limited to pendent group changes

Polyethylene Glycols (~1956)

$$HO - CH_2 - CH_2 - O - CH_2 - O - CH_2 - OH_2 - O$$

Drawbacks

- Active hydroxyl (-OH) groups at polymer termini allow a back-biting reaction
 - Results in phase degradation
 - Contributes to column bleed
- Very limited chemical modifications possible
- Limited to 280 °C maximum temperature

R = methyl, phenyl, fluoropropyl, and/or cyanopropyl (listed from least polar to most polar).

x,y = percentage in the overall polymer composition.

n = number of monomer repetitions to make the overall polymer.

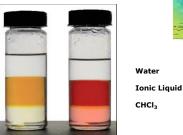
sigma-aldrich.com/il-gc



Most recent technology development

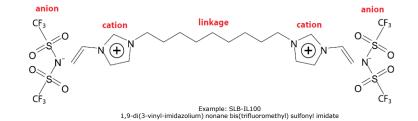
Ionic Liquid (IL) GC Columns

- Ionic Liquids are the newest phase type in GC ٠
- They are unique to Merck/Sigma-Aldrich
- Properties that make them desirable as GC stationary phases
 - remain liquid over a wide temperature range (Room Temperature→350°C)
 - highly polar nature (exceed polarity range of common polymeric phases)
 - broadest range of solvation interactions of any known solvent
 - good thermal stability
 - easily tailored to provide different polarities/selectivities
- Unique selectivity & polarity enabling separations not • possible with traditional phases
- Product line: •
 - SLB-IL columns
 - Newest addition, Option for GC
 - Watercol GC columns for water determination
 - i-Series selectivity & inertness





Source: Prof. Jared Anderson, University of Toledo, USA



- SLB-IL59 (3)
- SLB-IL60 (7)
- SLB-IL61 (3) B-IL76 - (3)
- B-IL82 (3)
- SLB-IL100 (7)
- SLB-IL111 (6)
- SLB-ILD3606 (3)



GC Column Polarity Scale Description of our Procedure

- Each column is characterized with a series of five probes plus several n-alkane markers to determine the retention index for each probe
 - Benzene
 - Butanol
 - 2-Pentanone
 - Nitropropane
 - Pyridine
- McReynolds Constants are then calculated using the retention index data of the column relative to the retention index data for the same five probes on squalane, the most non-polar GC stationary phase
- The five McReynolds Constants are summed to obtain Polarity (P) values, which are then normalized to SLB-IL100 (set at P=100) to obtain Polarity Number (P.N.) values

Our procedure was proposed by Prof. Luigi Mondello (University of Messina, Italy).

sigma-aldrich.com/il-gc



GC Column Polarity Scale Experimentally Determined Polarity Numbers

	McReynolds Constants						
Column	Benzene	n-Butanol	2-Pentanone	Nitropropane	Pyridine	Р	P.N.
SPB-Octyl	17	-20	6	19	6	28	1
Equity-1	11	10	33	60	16	130	3
SLB-5ms	33	30	55	91	43	252	6
SPB-20	76	79	104	167	109	535	12
Equity-1701	82	131	150	233	136	732	16
SPB-35	175	113	151	225	175	839	19
SPB-50	154	134	176	266	218	948	21
SPB-225	233	342	342	501	375	1793	40
PAG	276	459	320	508	428	1991	45
SUPELCOWAX 10	334	509	375	601	505	2324	52
SLB-IL59	338	505	549	649	583	2624	59
SLB-IL60	362	492	525	679	564	2622	59
SLB-IL61	371	551	516	624	648	2710	61
SP-2330	469	663	608	859	712	3311	75
SLB-IL76	456	690	643	845	745	3379	76
SP-2331	495	674	622	856	735	3382	76
SP-2560	510	724	652	913	773	3572	81
SLB-IL82	532	676	701	921	808	3638	82
TCEP	622	871	772	1072	957	4294	97
SLB-IL100	602	853	884	1017	1081	4437	100
SLB-IL111	766	930	957	1192	1093	4938	111

P (Polarity) = sum of the first 5 McReynolds Constants.

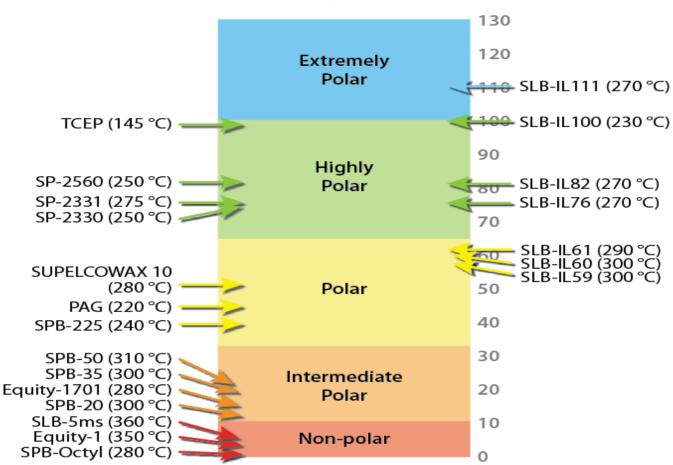
P.N. (Polarity Number) = Polarity (P) normalized to SLB-IL100 (set at P=100).

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GC Column Polarity Scale

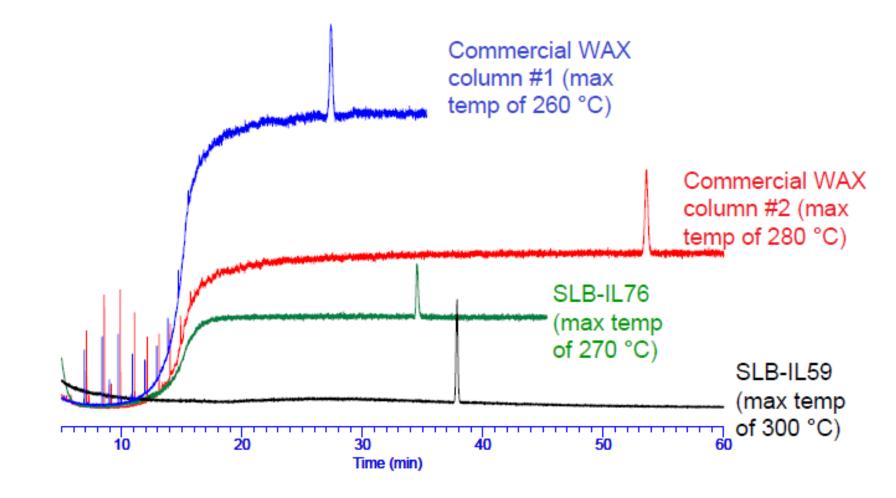
Visual Representation



On the left: Position/Maximum temperature classical GC phases. On the right: Position/Maximum temperature of Ionic Liquid GC phases.



Comparison of GC-MS TIC Bleed

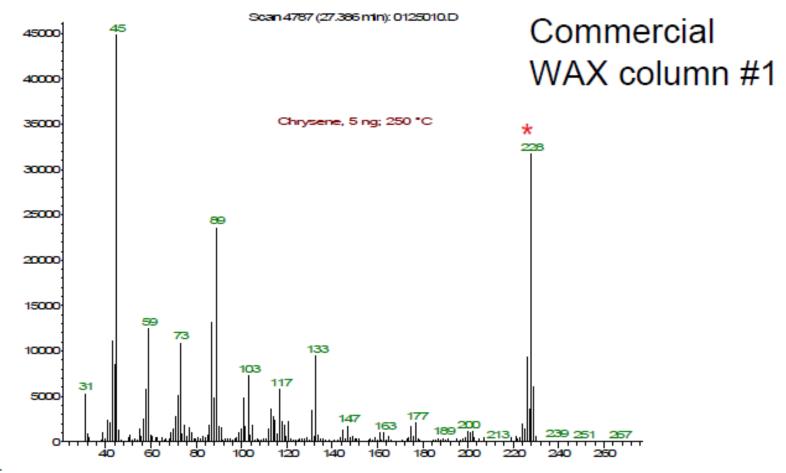


All TICs are on the same Y-scale



Mass Spectrum of Chrysene 5 ng on-column, Wax column, 250 °C

Abundance

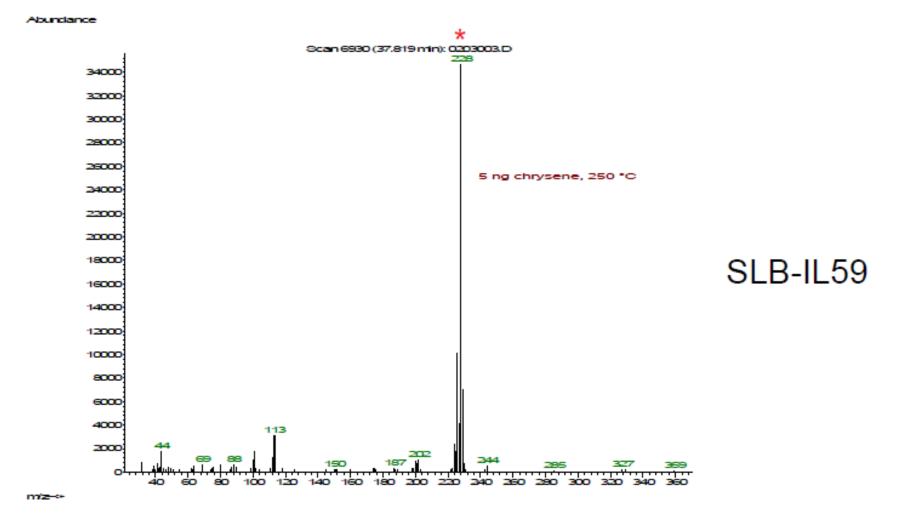


* Base peak in spectrum of chrysene



m/z⊸⊶

Mass Spectrum of Chrysene 5 ng on-column, SLB-IL59, 300 °C

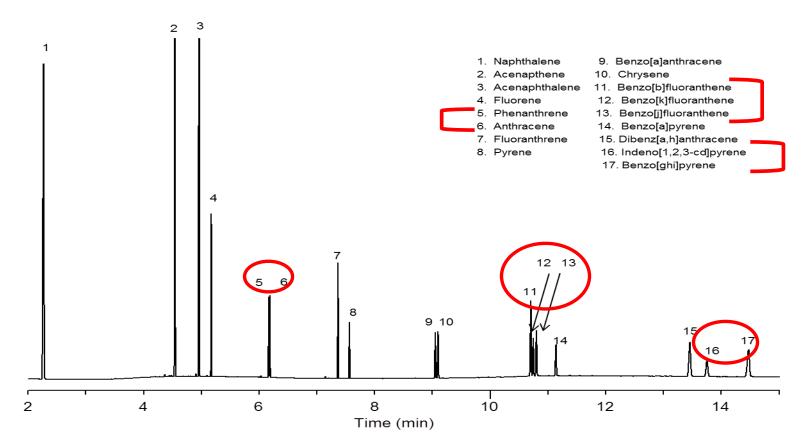


* Base peak in spectrum of chrysene



SLB IL-PAH

Selectivity and inertness to separate the PAHs specified under EFSA PAH4 with faster analysis time

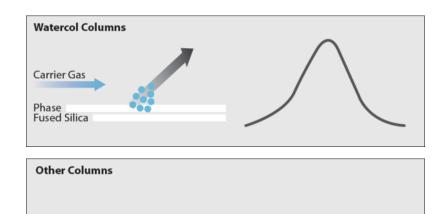




Watercol[™] -GC Columns

- Contain innovative ionic liquid stationary phases
 - highly polar but stable vs. water
 - produce a sharp peak shape for water providing:
- Qualitative and Quantitative Measurement of Water with GC (With appropriate detector like TCD, BID, MS, VUV)
- Show narrow peak widths and optimal peak heights also for many other small polar analytes.





Water determination with a GC is a new routine use option of a GC Instrument

Carrier Gas

Phase Fused Silica

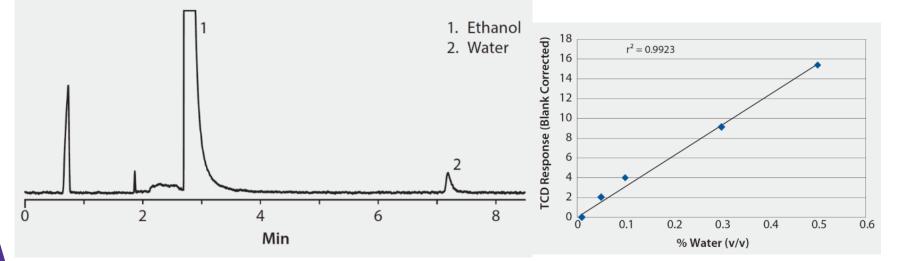
sigma-aldrich.com/watercol



Water Determination with Watercol 1910 Watercol – Water determiantion with GC

column: Watercol 1910, 30 m × 0.25 mm I.D., 0.20 μ m (29711-U) oven: 80 °C (10 min) inj. temp.: 250 °C detector: TCD, 200 °C carrier gas: helium, 26 cm/sec injection: 0.5 μ L, 100:1 split liner: 4 mm I.D., split type, cup design sample: water at 0.05% (v/v) in ethanol

sample: 5 standards, water at 0.01, 0.05, 0.1, 0.3, and 0.5% (v/v), in ethanol





Watercol Series Capillary GC Columns

Key Benefits of a Sharp Water Peak Shape

- Measurement of water
 - qualitative and quantitative
- Linear response over a very wide range (0.01% water to 100% water)
- Great sensitivity
 - 100 ppm using a thermal conductivity detector (TCD)
 - Anticipate much better sensitivity with
 - A mass spectrometer (MS) operated in the SIM mode
 - Vacuum ultraviolet (VUV) absorption spectroscopy
 - A barrier discharge ionization detector (BID)
- Reproducibility, virtually no change in column performance over time

NOTE: The detector being used must be able to detect water. sigma-aldrich.com/watercol

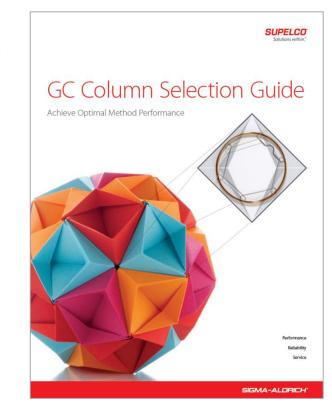




Column Selection Guide (KCX) Recommendation Page

Supelco Capillary GC Columns with Comparable Columns from Other Manufacturers

Supelco	Agilent®	Grace	Macherey-Nagel	Phenomenex*	Restek	SGE	Varian
Traditional (phases	by increasing phase	e polarity)					
Petrocol+ DH Octyl	-	-	-	-	-	-	-
SPB*-Octyl	-	-	-	-	-	-	CP-Sil 2 CB
SPB-HAP	-	-	-	-	-	-	-
Petrocol DH 50.2	DB-Petro, HP-PONA	. —	-	-	-	BP1 PO NA	-
Petrocol DH	DB-Petro	AT-Petro	-	-	Rtx-1PO NA	BP1 PO NA	CP-Sil PONA CB
Petrocol DH 150	-	-	-	-	-	-	-
Petrocol 2887, Petrocol B(2887	DB-2887	AT-2887	-	-	Rtx-2887	-	CP-SimDist
SPB-1 SULRUR	-	AT-Sulfur	-	-	-	-	CP-Sil 5 CB for Sul fur
Equity-1, SPB-1	DB-1, HP-1	AT-1	Optima-1	ZB-1	Rtx-1	BP1	CP-Sil 5 CB
SLB-5ms	DB-Sms, HP-Sms	AT-Sms	Optima-5 NS	ZB-5ms	Rtx-55il N.S.	BPX5	VF-Sms
NET-Biodiesel	-	-	-	-	NXT- BiodieselTG	-	Select Biodiesel for Triglycerides
HT-S (aluminum clad)	DB-Sht	-	-	ZB-Sht	-	HT-5	VF-Sht
PTA-S	-	AT-Amine	-	-	Rtx-5 Amine	-	CP-Sil 8 CB for Amines
SAC""-5	-	-	-	-	-	-	-
Equity-5, SPB-5	DB-5, HP-5	AT-5	Optima-5	ZB-5	Rtx-5	BP5	CP-Sil 8 CB
SPB-624	DB-624, DB-VRX	AT-6,24	Optima-6,24	ZB-6,24	Rtx-624	BP624	CP-Select 6,24 CB
0VI-G43	HP-Fast Residual Solvent	-	-	-	Rtx-G43	-	-





Column Selection Guide (KCX) Recommendation Page

Food and Beverage Indu	stry	L
	SPB®-Octyl SPB®-Octyl SPB®-Octyl SPB®-Octyl SPB®-Sm s MET-Biodiesel SAC®-5 SPB-624 VOCOL® SPB-624 VOCOL® SPB-628 SPB-628 SPB-608 SPB-608 SPB-608 SPB-200 SPB-205 SPB-205 SPB-1000 Omegawax® SPB-1000 Omegawax® SLB-IL59 SLB-IL59 SLB-IL59 SLB-IL59 SLB-IL59 SLB-IL50 SPP-2331 SP-2330 SLB-IL50 SPP-2331 SP-2331 SPP-000 SLB-IL111 Chial* Carboxen-1006 PLOT Supel-Q** PLOT Alumina sulfate PLOT Alumina chloride PLOT Alumina chloride PLOT SPB-201 SPB-000 SP-2331 SP-2331 SP-2331 SP-2331 SP-2331 SPB-000 SLB-IL59 SLB-IL50 SPP-2331 SPP-000 SLB-IL59 SLB-IL50 SPP-2331 SPP-000 SLB-IL50 SPP-2331 SPP-000 SLB-IL59 SLB-IL59 SLB-IL59 SLB-IL59 SLB-IL59 SLB-IL59 SLB-IL50 SLB-IL59 SLB-IL50 SLD-IL50 SLB-IL50 SLB-	Mol Sieve 5 A PLOT
Sugars as Alditol Acetates	• •	
Free Fatty Acids	••	
FAMEs by Boiling Point Elution	•	
FAMEs by Degree of Unsaturation	• • •	
Omega 3 and Omega 6 FAMEs	• • •	
cis/trans FAME Isomers		
Fatty Acid Ethyl Esters (FAEEs)		
Mono-, Di-, Triglycerides		
Sterols, Aliphatic Alcohols, Waxes		
Amino Acids		
Nutraceuticals, Antioxidants		
Organic Acids	• • • • •	
Flavois & Fragrances, Aroma	••	
Preservatives		
Pesticide Residues	• ••	
Veterinary Drug Residues		
Allergens	•	
Dioxins, Furans, PCBs		
Phthalate Esters		



Resources Complementary Pieces

- "Applications"
 - Includes multiple chromatograms across many industry types
 - Analyte IDs and GC conditions are included in the speaker notes for most
- "Bibliography"
 - Peer-reviewed journal articles leading up to and beyond the seminal 2005 JACS (Journal of the American Chemical Society) article
 - Updated periodically



Both pieces can be downloaded from < sigma-aldrich.com/il-gc-lit>.

sigma-aldrich.com/il-gc



Summary Ionic Liquid GC

GC phases based on Ionic Liquids:

- have a different selectivity compared to conventional phases
- allow for shorter analysis times
- provide lower bleeding and long lifetime
- Offer a broader temperature range compared to conventional polar phases
- Improve multidimensional separations (orthogonal selectivity and high thermal stability of polar phase)



03 Accessories



GC Accessories

Besides packed and capillary GC columns we offer a comprehensive range of GC accessories around the instruments:

GC Instrument Accessories

- Liner, Injector Septa, Ferrules, Fittings
- Syringes, Vials

Gas Management

- Gas Generators, Gas Purifiers
- Tubing, Valves & Pressure Regulators, Flow Meter



sigma-aldrich.com/gc



SUPELC

Maximize Performance!

Accessories: Syringes from Leading Manufactures

• Syringe is the introduction of the sample into the GC Injector port

Syringes from Leading Manufactures

- Hamilton
- SGE
- VICI Precision Sampling



In Supelco Catalog are more than 30 pages for syringes and spare parts





Vials - Overview

Vial

- Volume (with / without insert)
 - 1,5-2 mL for liquid inj.
 - 5-20 mL for headspace
- Neck style Screw, snap or crimp,
 - large or narrow opening
- With marking spot, graduated
- Clear or amber, glass or plastic

Сар

- · Solid or with hole
- Plastic or Metal (Aluminium or Magnetic)

Septa type

- PTFE/Silicon
- Rubber

Fit for Autosampler tray and handling







Insert







Standard Screw Neck

Short Thread leaves Space for robotic arms















Vials: Compatibility with Autosampler

http://www.sigmaaldrich.com/analytical-chromatography/analyticalproducts.html?TablePage=17533773

Popular Au	utosamp	ler Vials by I	nstrun	nent										
	Glass	Features	Cat. No.	Pk. Size	Page	Agilent 1050/1090	Agilent 1100	Agilent 7673A, Series I, II	CTC LC PAL	CTC GC PAL	Merck/Hitachi, AS/4000	PerkinElmer Autosystem and Clarus 500	PE ISS-100, 200, Integral 4000 and Series 200	Shimadzu GC Autosamplers
Crimp Top Vials														
6 x 32 mm	clear	tapered bottom	27283	100	19			\checkmark		\checkmark				
7 x 30 mm	amber	conical	27312	200	19			\checkmark						
7 x 32 mm	amber	round bottom	27314	100	19			~						
7 x 40 mm	amber	conical bottom	24744	100	19									
8 x 40 mm	clear	flat bottom	33321U	200	20									
12 x 32 mm	clear	PTFE/red rubber	29124-U	100	17	1	~	1	~	~	1	1	~	\checkmark
	clear	PTFE/silicone	29125-U	100	17	1	1	~	~	~	1	1	~	\checkmark
	amber	PTFE/red rubber	29127-U	100	17	1	1	1	~	~	1	1	~	\checkmark
	amber	PTFE/silicone	29128-U	100	17	1	1	~	~	~	1	1	~	~
Screw Thread, 12 x 3	32 mm													
Certified Vials, 9 mm thread	clear	PTFE/silicone	29381-U	100	6	1	1	~	~	~	1			~
	clear	PTFE/Silicone w/slit	29384-U	100	6	1	1	~	~	~	1			~
	amber	PTFE/silicone	29386-U	100	10	1	~	1	~	1	1			1
	amber	PTFE/Silicone w/slit	29387-U	100	10	1	1	1	1	1	1			1
Center Drain Vials	clear	PTFE/silicone	29307-U	100	13	1	1	1	1	1	1			~
	clear	PTFE/Silicone w/slit	29309-U	100	13	1	1	1	1	1	1			~
	clear	PTFE/silicone/PTFE	29308-U	100	13	1	1	1	1	1	1			~
	amber	PTFE/silicone	29313-U	100	13	1	1	1	1	1	1			1



Accessories: Vial Accessories

 There are always some easy to sell items coming with this product group:



CRIMP the vials!



Glass "Magnet" Holder – Don't work without it!



Take the cap off the vial!



Stack and Store them!



Gas Supply

Product Areas

- Gas generation
 - Gas generators, air compressors
- Gas delivery

Gas purification

 Polishing purifiers, contaminant traps (remove hydrocarbons, moisture, oxygen, carbon dioxide), gas purifiers (clean helium), filters (remove particles, oil)

Gas management & delivery

- Pressure regulators, flow regulators, leak detectors,
- Tubing, cutters, reamers, benders, fittings, shutoff valves

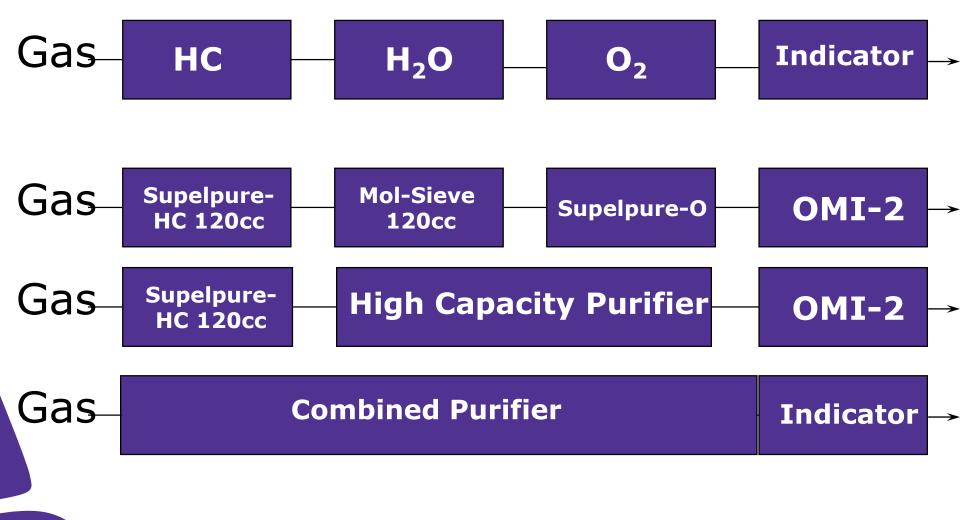
Visit sigma-aldrich.com/gaspurifiers for more information.

sigma-aldrich.com/gc



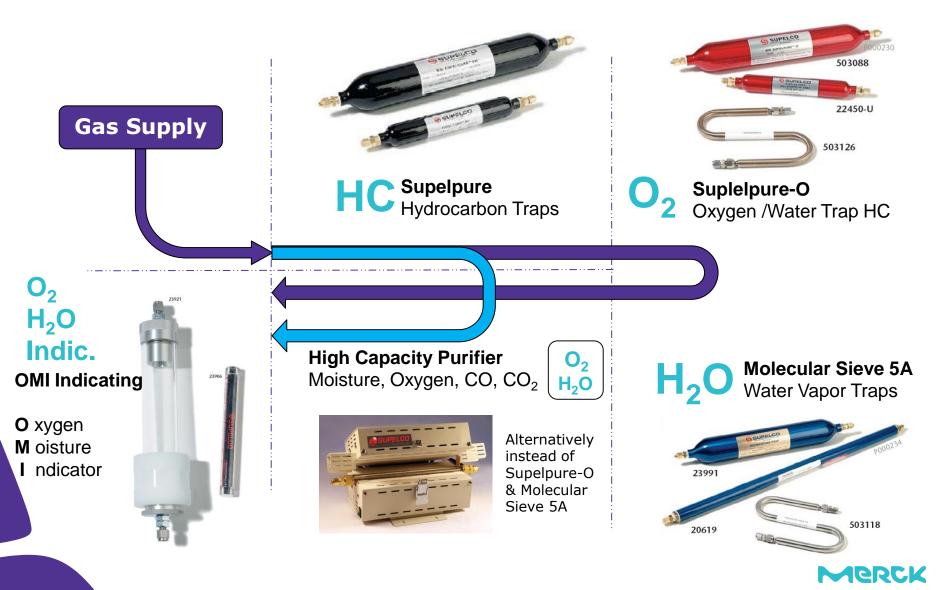


Carrier gas: What needs to be removed? Which order?





Purifier types – In Line



GC Accessories Maximize Performance! Brochure

28-page, 4-color, bundling brochure

Lists common replacement items...

• Septa, liners, ferrules, solvents, syringes, vials, purifiers, and much more

for several GC makes/models

 Agilent/HP, PerkinElmer, Shimadzu, Thermo, and Varian



A 'must-have' for all GC labs! You can request hard copies through the Sigma-Aldrich literature houses.



Summary GC by product type

- GC Columns
 - Packed
 - Capillary
 - Common phases (e.g. SLB-5ms, SLB-35ms)
 - Special Purpose (e.g. SP-2560, SP-23131, Petrocol)
 - Ionic Liquid (Newest Technology)
 - i-Series
 - Watercol
- Accessories
 - Fittings, Septa, Flow Meters, Column Installation
 - Vials & Syringes
 - Gas Supply & Gas Purification
- Applications
 - Varous fields of work (Envi, Food&Bev, Petrochem...)

Complementary products

- GC Solvents
- Sample Preparation
 - SPE, SPME, Extraction
- Standards
 - (Certified) Reference Materials
 - Proficiency testing



Thank you for your attention!

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