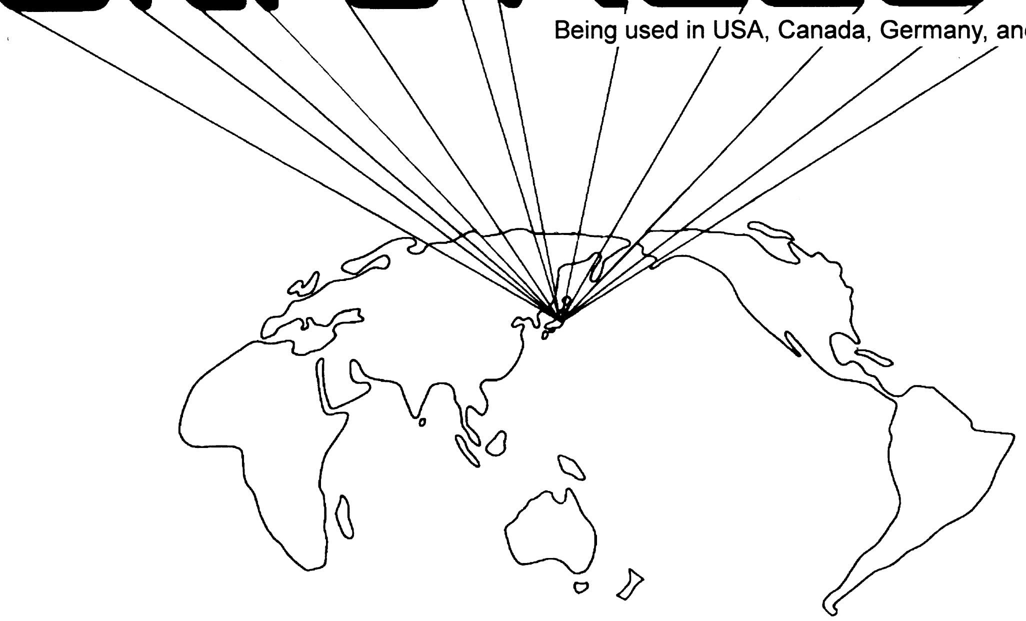
FRONTIER LAB

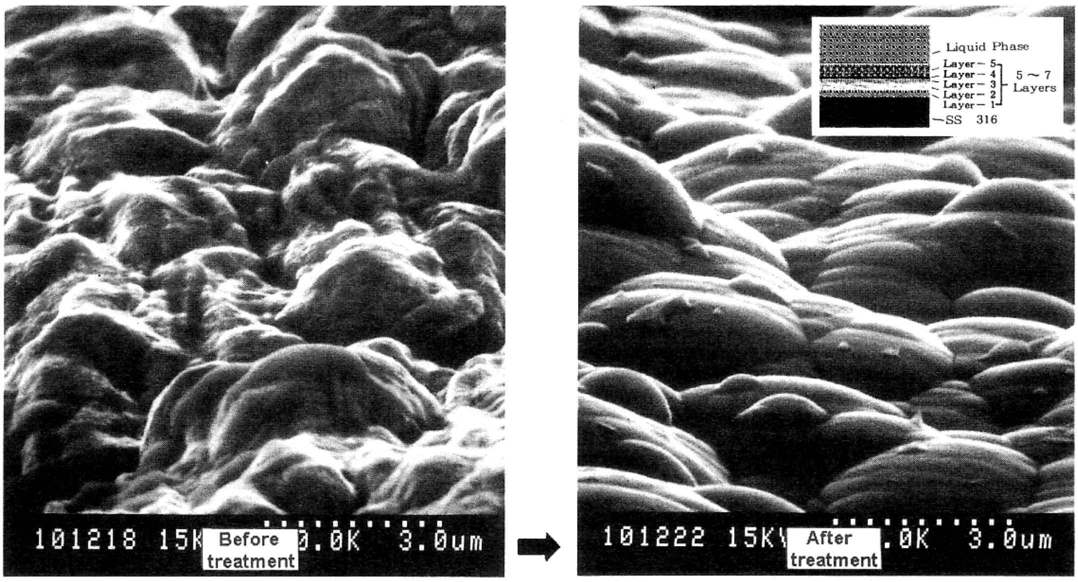
Stainless Steel Capillary Column

Ultra ALLOY®

Being used in USA, Canada, Germany, and Korea



A Model Of An Ultra ALLOY® Capillary Column



SEM Images of stainless steel column surface before and after multi-layer pretreatment

Capturing World Attention! Employed by NASA!

Ultra ALLOY® Capillary Columns

Stainless Steel or Fused Silica?

Employing a slanted-multi-layer structure on a Stainless Steel (SS) column surface, Ultra ALLOY® capillary columns have been paid much attention, and are replacing conventional columns based on fused silica (FS), which has been considered as the ultimate material. The following ten Q&A's feature the high performance.

Q1: Capillary columns have evolved from Golay (SS) column, then to glass, and to FS. Why SS column now? What is the difference between FS and SS besides the materials? Please describe it using a methylsilicone column as an example among many others.

Your concern is very natural. Although we have developed the columns, there are some areas that we cannot explain. Iron atoms in SS are known to adsorb hydrocarbons and polar components. However, if the surface can be completely covered by an inert layer, SS will be an ideal material for capillary columns. Because SS is a metal, it has high flexural, abrasion, impact, and thermal resistances. Use of SS and our advanced proprietary column pretreatment technology have made it possible to develop the Ultra ALLOY® columns and we are the center of world attention.

Q2: How was the metal surface pretreated?

We have succeeded in forming a multi-layer structure (5-7 layers each less than 0.001 micron) on the surface of SS column as shown in the SEM pictures in the front cover page (patent applied for). These layers are chemically bonded to each other, and the chemical structure of the top layer can be modified depending on the kind of liquid phase. We wanted to limit the number of layers to 3, but we found at least 5 layers were required in order to outperform the FS column performance. Our top grade columns have 7 layers to provide highest inertness.

Q3: What about the absorption of primary amines which are known to be the problems with ODS columns used in HPLC? Is the analysis difficult with FS columns due to tailing problems?

That's a hard question. Only Hewlett Packard, known to supply high performance products, has done the tests on this. We have challenged them with Ultra ALLOY®-1. Fig. 1 shows the performance comparison with Brand (J). When 5mg of a sample was used in heating program mode, ours clearly outperforms. The pyrolysis of Nylon-12.6 is known to give peaks due to various amines, shown in Fig 5. These peaks are extremely difficult to separate with FS columns.

Q4: The internal surface of a SS capillary column has less than 10µm (peak to valley) roughness. The thickness of liquid phase at the peak is small, while that at the valley is large. Does this affect peak separation?

Yes, it does. As the liquid phase becomes very thin, the top layer of the slanted 5 layer structure emerges, causing problems. We found 3 layer surface pretreatment of the SS column to be inadequate due to the effects from the metal surface; therefore, 5 layer pretreatment was necessary to solve the problem. The coating efficiency is about 90% and is comparable to FS columns. The SEM picture shown in the front cover page clearly shows the improved surface structure.

Q5: I hear that Ultra ALLOY® columns have high thermal stability; however, I rarely heat up to 250°C. I do not think such high temperature stability is necessary, because I thoroughly pretreat samples before analysis. Does it still have any advantages?

Yes, it does. Advantages of high thermal stability of a column are: (1) low bleeding and high durability; (2) protection against column degradation by nonvolatiles from samples; (3) cleaning of columns without use of solvents and guarding against ghost peaks - allowing great time saving; and (4) high data reproducibility over extended period of time.

Samples normally contain a minute amount of nonvolatile species as impurities. Such species deposit over the column inlet or the entire column, they can act as the liquid phase and cause peak broadening and adsorption. Triglycerides and mineral oil are the common high boiling impurities, and they can be eluted off the column by baking at high temperatures (380-400°C). Cumbersome solvent cleaning steps (removing column, cleaning, drying, mounting column, and baking) are not required, if columns are baked at the end of a day. Another advantage is that it is effective in reducing ghost peaks due to high boiling species remained in the column, leading to great saving of analysis time. The high degree of durability means that the analysis is reliable and the data are reproducible over an extended period of time. Fig. 2 shows a comparison of column degradation by blending 5% rapeseed oil in a sample. The internal surface area of our SS columns is 10-20 times greater than that of FS columns; thus, oil components are difficult to diffuse. As a result, SS columns have high resistance against contamination.

Q6. Is the lot-to-lot reproducibility good?

Yes, it is. Ultra ALLOY® columns are quality checked by retention indices, partition ratios, coating efficiency, and the use of polar species for inertness. Table 1. shows the reproducibility of the columns.

Q7: How small can a column be coiled? We would like to condense a sample using a liquid nitrogen trap. FS Megabore columns cannot be coiled so small in diameter.

You have come up with a good application. If SS columns are coiled slowly, the diameter can be as small as 1 cm. Columns with 0.25 mm inner diameter can be clogged by moisture and solvent condensation, when concentrating sample at liquid nitrogen temperature, but ones with 0.5 mm inner diameter should work without problems. (See Fig. 7 for an example)

Q8: What polar columns do you have?

There are a variety of polar columns available as tabulated in the last page. See application examples. Liquid phases used in packed columns are available in Ultra ALLOY® columns. Please ask for details. PyGC, triglyceride and PEG20M (with KOH) columns are also available for specific applications.

Q9: What precautions do you recommend for GC/MS applications?

With a quadruple type MS, the column outlet can be inserted to the ion source, but with a magnetic type, a jet separator should be used, or alternatively, a length (50 cm) of a FS column (P/N:PY1-2210) should be connected at the column outlet.

Q10: I have seen SS columns internally coated with fused silica in the U.S. If bent, do you think the FS breaks and metal surface is exposed?

FS coating was considered in our lab at the early stage of development, but we found FS on the internal surface would break easily when columns were bent as you speculated Fig. 6 shows that a commercial FS coated columns becomes very active when the internal FS coating breaks and comes off from the metal surface, exposing the metal surface. Because of the reasons above, Frontier Lab does not employ the FS coating method, although the manufacturing cost is less. Currently our inert tubing is extensively used as an interface in various purge & trap TG/MS and GC/MS.

Table 1. Lot-to-lot Reproducibility (n=30 for each year)

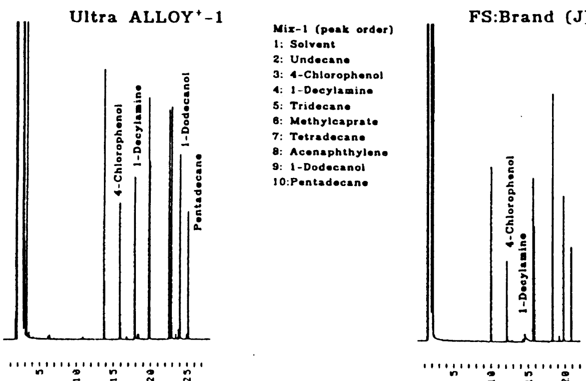
Column: UA-1(HT), 100% dimethylpolysiloxane, 30m (0.25ø), 0.15µm at 130°C

	1993		1994		1995	
	RI	CV (%)	RI	CV (%)	RI	CV (%)
Methylcaprate	1305.4	0.018	1305.5	0.017	1305.6	0.015
Acenaphthalene	1418.7	0.021	1419.1	0.022	1419.7	0.022
1-dodecanol	1456.1	0.009	1456.1	0.008	1456.0	0.006
Column Efficiency(%)	82.3	2.010	83.4	1.970	87.2	1.720

RI: Retention Index

Fig. 1. Activity Comparison of Ultra ALLOY®-1 and Fused Silica (FS) Columns

30m (0.25ø)0.25µm, programmed from 40°C to 220°C at 5°C/min



BASIC PERFORMANCE

- Applications featuring high inertness, high contamination resistance, high thermal resistance, low bleeding, and high durability -

Fig. 2. High Contamination Resistance (consecutive injection of a sample containing 5% rapeseed oil): UA⁺-1
10m (0.25ø) 0.25μm at 120°C, Split at 250°C

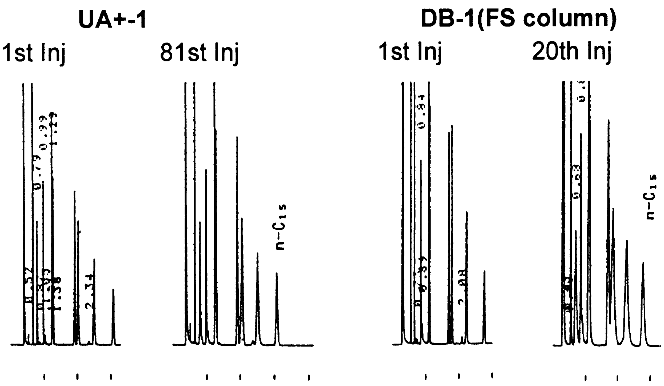


Fig. 3. Thermal stability (change in capacity ratio (k) upon continuous exposure to high temperatures)
Column: UA-DX30, UA-1(HT), 15m (0.25ø) 0.15μm (Because the stationary phases are physically bonded to the rough column internal surface as shown in the SEM picture in the front cover page, our products offer high maximum temperatures and durability.)

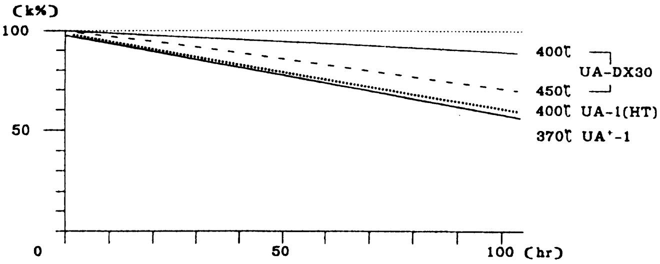


Fig. 4. Low bleeding (UA⁺-5: 6pA at 350°C)
15m (0.25mmø) 0.25μm at 70 to 350°C at 20°C/min, Split at 300°C

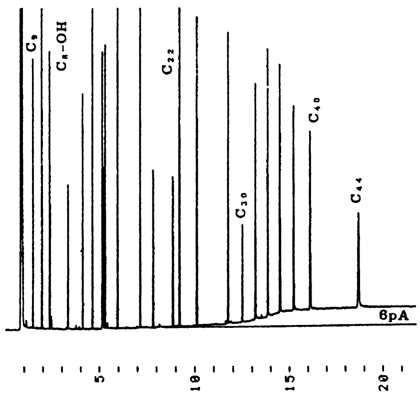


Fig. 5. Inertness (PyGC of Nylon 12-6): UA-PY2
(Various primary amines from pyrolysis are eluted off) Pyrolysis at 550°C, 30m (0.25ø) 0.5μm, 40-360°C at 5°C/min, Split at 300°C

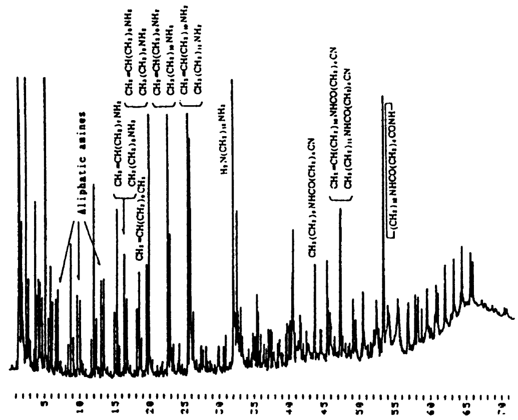


Fig. 6. Comparison with USA products: UA⁺-5
(Column activity with a coiled column at the inlet (3 turns / 3cm in diameter) With Column (B) polar species are adsorbed when the internal silica coating came off. 15m, 0.5μm at 120°C. Sample is the same as in Fig. 1.

(A): UA⁺-5, 0.5ø

(B): Metal column from other supplier, 0.53ø

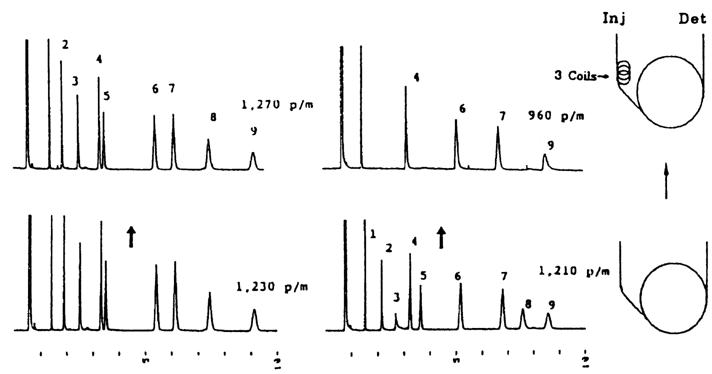
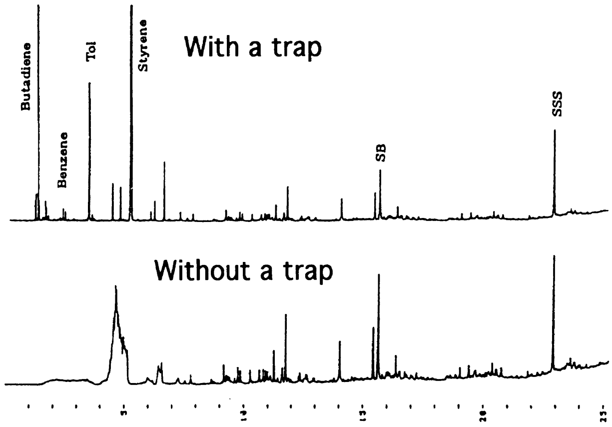


Fig. 7. Use of gas trap: UA⁺-1
(A length of a column at the edge was coiled (2cm in diameter) and was immersed in liquid N2. Evolved gases from pyrolysis were trapped for 10min) 30m (0.25ø) 0.5μm, 30 to 250°C at 10°C/min

Evolved gases from styrene butadiene copolymer
(200 to 400°C at 20°C/min)



APPLICATIONS OF NEW PRODUCTS

- UA-502 and UA-624 are used by NASA -

Fig. 8 A trace amount of agricultural chemicals: UA+-1(S)
15m (0.25ø)0.25µm, 60 to 320°C at 15°C/min

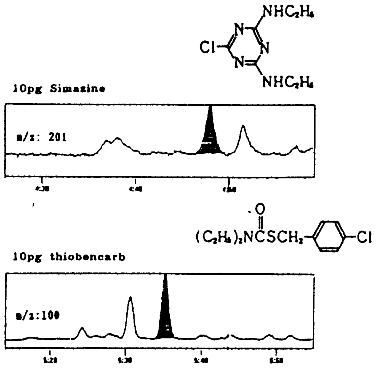


Fig. 9 Wax: UA-DX-30
15m(0.5ø)0.15µm, 50°C to 440°C at 20°C/min, On-column

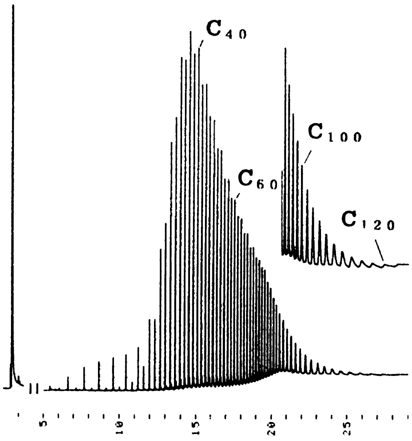


Fig. 10 A trace amount of nicotines: UA-CW(KOH)
(Effective for basic species), 5m(0.25ø) 0.25µm, 50 to 220°C at 20°C/min

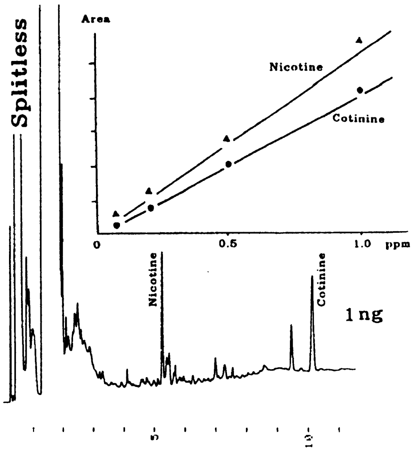


Fig. 11 Triglyceride: UA+-65/UA-DX30
Column: 300 to 350°C at 20°C/min, then conditions shown below used (split).

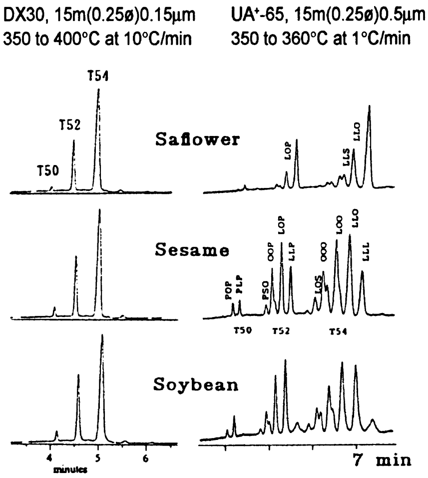


Fig. 12 Phenols: UA-DIDP
(Separation of 2,4- and 2,5-xylenols), 30m (0.25ø) 0.25µm, 130°C

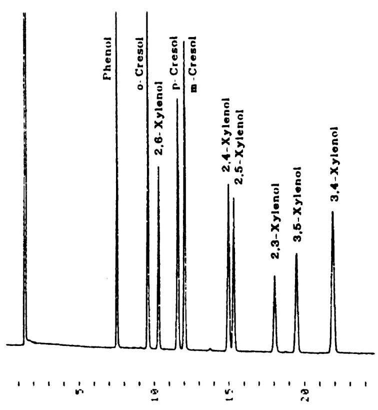


Fig. 13 Aliphatic esters: UA-Sil 10C
(Isomer separation by very polar liquid phase column) 30m(0.25ø) 0.2µm, 140°C to 200°C at 2°C/min

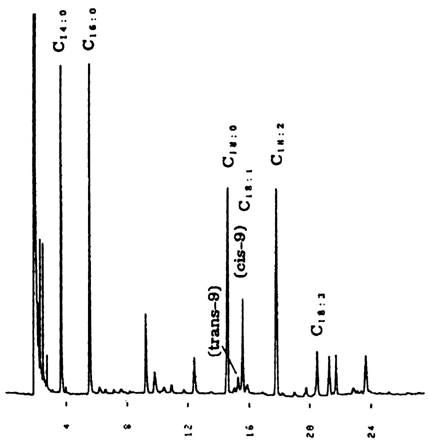


Fig. 14 Column used by NASA: UA-502
(The column is recoiled into 3cm diameter, and will be used in a space shuttle.) 60m(0.5ø)3µm, 40°C hold for 12min, then to 150°C at 6°C/min

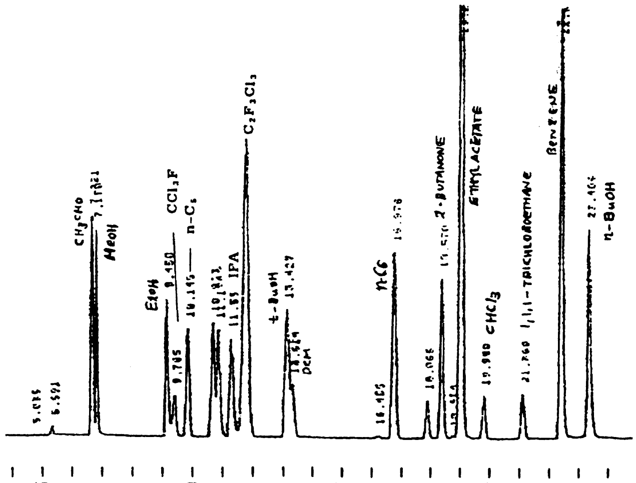
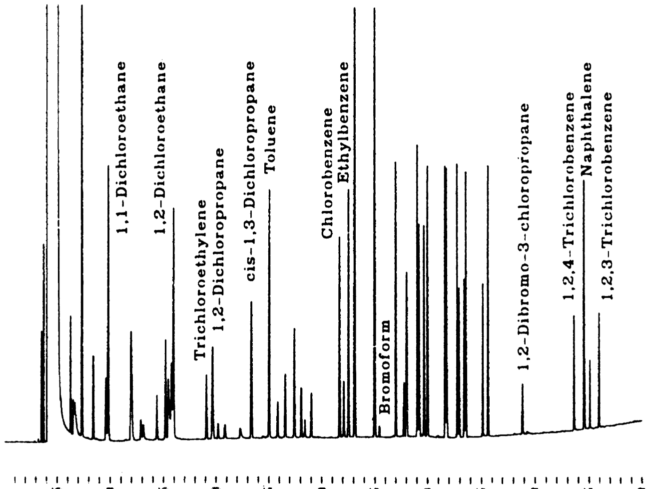


Fig. 15 Volatiles in drinking water: UA-624
(1/10 of bleeding compared to other supplier's in GC/MS applications, this is gaining popularity among users), 60m (0.25ø) 1µm, 10min hold at 30°C, then to 200°C at 3°C/min



OTHER APPLICATIONS

Fig 16 GROB test standard: UA⁺-1 , UA-CW
15m (0.25ø) 0.25μm, split at 250°C, (3min hold at 60°C, then to 200°C at 5°C/min)

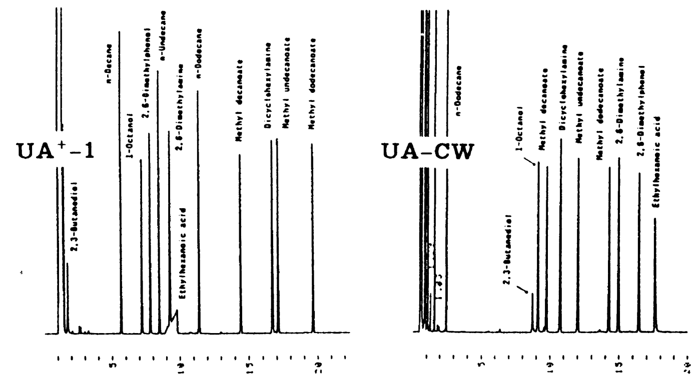


Fig. 17 Agricultural chemicals used on a golf course: UA⁺-1 (S)
15m (0.25ø) 0.25μm, split at 250°C, (70°C to 300°C at 5°C/min)

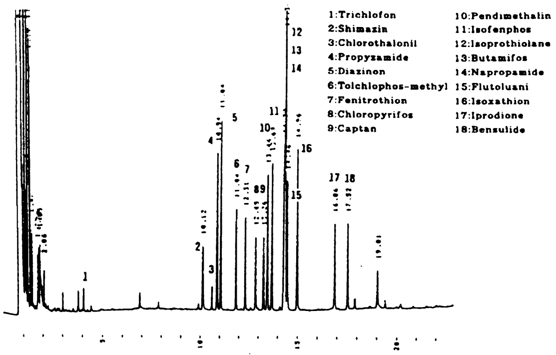


Fig.18 Ethanol amines: UA⁺-1
15m (0.5ø) 5μm, split, 50 to 230°C at 20°C/min

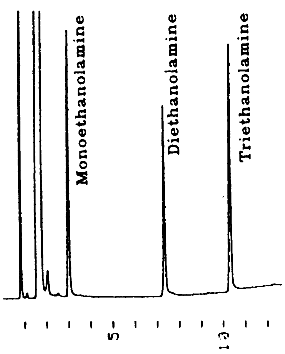


Fig.19 Multifunctional alcohols:
UA-CW, 15m(0.25ø) 0.25μm, 80 to 200°C at 20°C/min

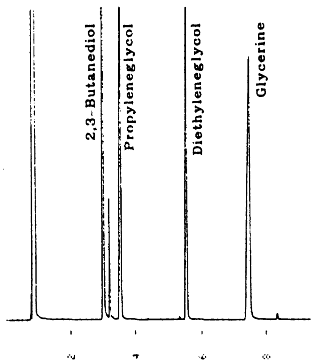
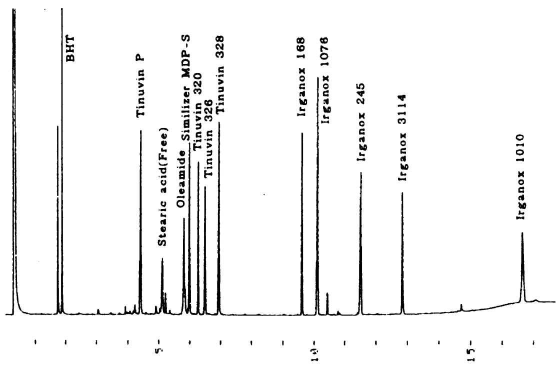


Fig. 20 Polymer additives: UA-PY3
10m(0.25ø) 0.15μm, 100 to 420°C at 20°C/min, Split at 380°C



Ultra ALLOY® Capillary Column Specifications

Inner diameter (Outer diameter) : 0.25(0.47) / 0.53(0.75)mm, Material : SUS 316

Column		Stationary Phase	Polarity	Application	Max Temp (Prog)	Replacement
Premier Grade	UA-1(MS/HT)	dimethyl polysiloxane	None	High boiling species, general purpose(low breed)	450(420ºC: 0.5µm)	DB1-MS/HT
	UA$^+$-1(HT)	dimethyl polysiloxane	None	High boiling species, general purpose	420	DB1-HT
	UA-5(MS/HT)	5% diphenyldimetyl polysiloxane	Ext.low	High boiling species, general purpose(low breed)	430(420ºC: 0.5µm)	DB5-MS/HT
	UA-DX30	carborane-siloxane (Dexsil 300)	Ext.low	High boiling species, waxes	450	-----
Regular Grade	UA$^+$-1	dimethyl polysiloxane	None	General purpose	380 (*1)	DB-1ms
	UA$^+$-5	5% diphenyldimetyl polysiloxane	Ext.low	General purpose	380 (*1)	DB-5ms
	UA$^+$-65	65% diphenyldimetyl polysiloxane	High	Triglycerides, pharmaceuticials, agricultural chemicals	380	-----
	UA-CW	polyethylenglycol 20M (PEG20M)	High	Polar species, general purpose, solvents	260 (*1)	DB-WAX
	UA-PY3	dimethyl polysiloxane	None	Pyrolysis GC, additives, high boiling species	420	-----
Appli-cation Specific	UA-PBDE	dimethyl polysiloxane	None	Brominated flame retardants, PBDE	380	-----
	UA-SIMDIS(HT)	dimethyl polysiloxane	None	Simulated distillation, high boiling species, waxes	450	-----
	UA-624	6% cyanopropylphenyl polysiloxane	Medium	VOC analysis (purge & trap)	270	DB-624
	UA$^+$1(S)	dimethyl polysiloxane	None	Trace analysis, agricultural chemicals	370	-----
	UA-PY1	dimethyl polysiloxane	None	Pyrolysis GC (medium to high boiling species)	390	-----
	UA-PY2	dimethyl polysiloxane	None	Pyrolysis GC (low to high boiling species)	380	-----
	UA-5(P)	5% diphenyldimetyl polysiloxane	Ext.low	Phenol (endocrine disrupting chemicals)	380	-----
	UA$^+$-50	50% diphenyldimethyl polysiloxane	Medium	Pharmaceuticials, agricultural chemicals, steroids	390	DB-17
	UA$^+$-1701	14% cyanopropylphenyl polysiloxane	Medium	Solvents, alcohol, agricultural chemicals, sugars	320	DB-1701
	UA-Sil10C	cyanopropyl (Silar 10C)	Medium	Aliphatic acids	280	-----
	UA-FFAP	PEG20M: nitro-TPA ester	High	Aliphatic acids, aldehydes, ketons	260 (*1)	DB-FFAP
	UA-CW(KOH)	PEG20M (KOH treatment)	High	Trace amines	260	-----
	UA-TRG	65% diphenyldimetyl polysiloxane	High	Triglycerides	380	-----
	UA-DIDP	di-isodecylphthalate	High	Phenol isomers	150	-----
Special Purpose	UADTM	dimethyl polysiloxane (deactivated)	None	Interfaces	450	

(*1): Normally 20-50ºC lower for films thicker than 1µm.

Inner Diameter, Film Thickness and Length

Column		i.d. 0.25 mm	i.d. 0.53 mm	Length (m)				
		Film Thickness (µm)		5	10	15	30	60
Premier Grade	UA-1(MS/HT)	0.1 0/ 0.25 / 0.50	----------	---	---	✓	✓	---
	UA$^+$-1(HT)	----------	0.10 / 0.15 / 0.25	---	---	✓	✓	---
	UA-5(MS/HT)	0.10 / 0.25 / 0.50	----------	---	---	✓	✓	---
	UA-DX30	0.15	0.15	---	---	✓	✓	✓
Appli-cation Specific	UA-PBDE	0.05	----------	---	---	✓	---	---
	UA-SIMDIS(HT)	----------	0.10	✓	✓	---	---	---
	UA-624	1.00	3.00	---	---	---	✓	✓
Regular Grade	UA$^+$-1	0.25 / 0.50 / 1.00	0.25 / 0.50 / 1.50 / (5.00)*3	---	---	✓	✓	✓
	UA$^+$-5	0.25 / 0.50 / 1.00	0.25 / 0.50 / 1.50 / (5.00)*3	---	---	✓	✓	✓
	UA$^+$-65	0.10	0.10	---	---	✓	✓	✓
	UA-CW	0.25	1.00	---	---	✓	✓	✓
	UA-PY3	0.10	----------	---	✓	---	---	---
Products by Order (*2)	UA$^+$-1(S)	0.25 / 0.40	0.25	---	---	✓	✓	---
	UA-PY1	0.25	----------	---	---	---	✓	---
	UA-PY2	0.50	----------	---	---	---	✓	---
	UA-5(P)	0.25	----------	---	---	---	✓	---
	UA$^+$-1701	0.25 / 0.50 / 1.00	0.25 / 0.50 / 1.00	---	---	✓	✓	✓
	UA$^+$-50	0.10 / 0.25 / 0.50 / 1.00	0.25 / 0.50 / 1.00	---	---	✓	✓	✓
	UA-Sil10C	0.20	----------	---	---	✓	✓	✓
	UA-FFAP	0.25	0.50 / 1.00	---	---	✓	✓	✓
	UA-CW	----------	0.50	---	---	✓	✓	✓
	UA-CW(KOH)	0.25	0.50 / 1.00	---	---	✓	✓	✓
	UA-TRG	0.10	----------	---	---	✓	✓	---
	UA-DIDP	0.40	----------	---	---	---	✓	✓

(*2): Contact us for details. (*3) 5 µm thickness are not available for 60 m length.

Capillary Deactivated Tube

i.d. x o.d. (mm)	Polarity	5m	10m	Specification
		P/N	P/N	
0.15 x 0.47	None	UADTM-5N	UADTM-10N	**[Material]** SUS 316
0.25 x 0.47	None	UADTM-5M	UADTM-10M	
0.25 x 1.58 (1/16")	None	UADTM-5M16	UADTM-10M16	**[Film Thickness]** less than 0 .01 µm
0.32 x 0.75	None	UADTM-5MW	UADTM-10MW	
0.53 x 0.75	None	UADTM-5W	UADTM-10W	**[Deactivation]** dimethylpolysiloxane
0.53 x 1.58 (1/16")	None	UADTM-5W16	UADTM-10W16	
0.80 x 1.15	None	UADTM-5G	UADTM-10G	**[Min-Max Temp]** -196ºC to 450ºC
0.80 x 1.58 (1/16")	None	UADTM-5G16	UADTM-10G16	
1.20 x 1.58 (1/16")	None	UADTM-5E16	UADTM-10E16	

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