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Ultra ALLOY® Capillary Column Instruction Manual

Frontier Laboratories Ltd.

Thank you for purchasing Ultra ALLOY® capillary column (UA column). In comparison to conventional fused silica capillary column (FS column), the Ultra ALLOY® capillary columns offer excellent mechanical strength, inertness, max use temperature (thermal stability), and resistance to contamination. We recommend that you read this manual thoroughly in order to make the best use of these high performance columns. Note that the column performance is greatly deteriorated by contaminations in the flow path, low temperature spots in the joint between injection port and column, resulting in poor elution of high boiling compounds. If you have questions on UA columns, feel free to contact your local sales office or Frontier Laboratories.

Using Ultra ALLOY® capillary columns - - - from practical point of view - - -

In GC analysis, interferences from previous runs (ghost peaks) are common, and repeated analysis is often required. To avoid this problem, it is best to pre-treat samples; however, this is a time consuming process and time is usually limited. The UA columns have strong retention strength of liquid stationary phase to the rough inner wall of stainless steel column, and because of this the max use temperature is 50 to 80ºC higher than that of FS columns. Therefore, it is recommended that the UA columns be used in a manner described below.

- In a temperature programmed heating, the final temperature must be at least 40ºC below the max use temperature of the column, then at the end of analysis, rapidly heat the GC oven to near max use temperature to drive off residues from the column. This will help reduce interferences such as ghost peaks.

Table1 Part numbers of ferrules recommended for Ultra ALLOY® Capillary Columns

Column id. / Manufacturer	id. 0.25 mm column (od. 0.47 mm)		id. 0.53 mm column (od. 0.75 mm)	
	Injector side	MS side	Injector side	MS side
Agilent (6890, 7890)	5080-8853* 5062-3514	5062-3506	500-2118* 5062-3512	5062-3538
Shimadzu (2010)	221-32126-05* 670-15003-04	670-15003-04	221-32126-08* 670-15003-07	670-15003-07
Jeol (K9)	Use ferrule recommended for each GC	780304276	Use ferrule recommended for each GC	780304268
Thermo Fisher (DSQ II)	290VT187	29033497	290VT188	290MT231**
Other	Use ferrule with id. 0.5 mm recommended by manufacturer.		Use ferrule with id. 0.8 mm recommended by manufacturer.	

* Made of graphite.

** Made of SilTite. Contact manufacturer for details.

*** Other ferrules are mode of graphite-polyimide blends.

Note: The Frontier Labs GC/MS adapter is attached to the interface of a GC/MS system. The same nut and graphite ferrule used in GC-FID can be used; therefore, it is easier to use than before. Further, with this adapter installed, analysis can be performed at oven temperatures up to 400ºC without air leakage.

CAUTION The ends of column are very sharp, be sure to wear protective gears (safety goggles) when installing and uninstalling columns.

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1. Installing UA column

Installing an Ultra ALLOY® capillary column (UA column) to GC is basically the same as FS column. UA columns are featured by inertness, high thermal resistance, high lot-to-lot reproducibility, high mechanical strength, and resistance to contaminations.

1.1 Temperature setting for GC

Before starting to use a UA column, conditioning such as heating the column at its recommended max use temperature for one hour (if the film thickness is 0.5 µm or higher, use a 50ºC lower temperature than recommended temperature for 20 minutes) while the carrier gas is allowed to flow through the column is recommended. This will clean the GC system including the UA column. When the column is used at its max use temperature, set the detector temperature to the same temperature or 20ºC higher. Please note that if the detector temperature is lower than column temperature, the detector may get contaminated, resulting in unstable baseline and increased noise level. Set the injection port temperature to a proper one depending on your target analytes.

1.2 Installing column to GC

When the GC injector and detector temperatures are stable at set temperatures, follow the STEPs below to install a UA column. Ferrules used for each GC model are summarized in Table 1 of this manual.

STEP-1) Attaching GC column nut and graphite ferrule

Refer to STEP-5 for note on using graphite ferrules.

Note: Using the supplied file, cut off a length of 1 cm each of the inlet and outlet of the column only when ferrules have been attached.

STEP-2) Straightening column for inserting to detector

When the column is warped, straighten it as much as possible. Place the column between your index finger and thumb, bear down on the bent column several times.

STEP-3) Cutting off both ends of column (instruction for cutting column ends is included in the package.)

● Ends of column

After the column is passed through ferrule, the ends of column may be clogged with small pieces of graphite debris, cut the column ends by approximately 1 cm each using a triangular file. Using the edge of the file , apply force back and forth against the outer surface of the column at an angle of 30º to create a deep scratch, then apply the flat surface of the file to the other side of the column and bend the column a few times to cut the column end. Make sure that the cut surface is not excessively squeezed.

● Cut surface of column when using On-Column

When a column with id. of 0.53 mm is used, a sample can be injected directly into the column. When this method is used, the cut surface is particularly important. Check to see if a syringe needle can be smoothly inserted into the column inlet before attaching to the injector. It is almost impossible to make the column perfectly straight. It is quite normal that you sense some resistance when inserting syringe needle into the column inlet and there is no problem introducing sample to the column.

● Cut surface activity

The special treatment on the column inner surface is chemically and physical stable; therefore, there is no worry about delamination of stationary phase or active inner surface.

Note: Leave the cut surface as it is. Metal debris gets into the column if the cut surface is attempted to smooth using a file.

STEP-4) Setting carrier gas and make-up gas flow rates

● Checking carrier gas flow

Insert the column inlet to the GC injector, then immerse the column outlet into a volatile solvent to make sure the carrier gas is flowing. This is extremely important. If the column temperature is increased without carrier gas stream, the liquid phase of the column is easily decomposed by oxygen in air, making the column unusable in a worst situation. Take an extra caution when the column is heated to 200ºC or higher temperatures.

● Connecting to detector

The column outlet position in the detector is extremely important to prevent abnormal phenomenon such as peak broadening or absorption. Be sure to connect the column to the detector in reference to GC manual. Also, it is recommended that make-up gas be used at the column outlet. The make-up gas will make the detector dead volume small and increase detector sensitivity. See section 2.4 B of this manual for additional information.

STEP-5) Conditioning column and system

● Conditioning column

All UA columns are conditioned at the recommended max use temperature before shipping; however, in the case where abnormally high baseline is observed, it is recommended that the column be conditioned at the max use temperature for at least one hour while streaming carrier gas with column nut and graphite ferrule attached.

● Conditioning GC system

After a column has been installed and the flow of carrier gas has been confirmed, raise the GC oven temperature to the near max use temperature at a ramp rate of 5 ºC /min. If you do not want the detector to be contaminated, the column outlet should not be connected to the detector. Conditioning with the column outlet connected to the detector may degrade the detector performance by contamination, in particular this is true with detectors such as NP/FID and ECD. Refer to section 2.5 of this manual for detail.

● Conditioning graphite ferrule

Graphite ferrules are made by molding process and contain additives such as plasticizers, which can be the cause of bleed. It is recommended that new unused graphite ferrules be placed in a beaker and heated at 400ºC for four hours in an oven (in air) before using or storing. The major sources of bleed are graphite ferrule used at the FID connection (in the case of Agilent GC7890/6890, it is the graphite ferrule at FID and column connection.) and contaminations of septum, injector and detector. As shown in Fig. 1, bleed can be greatly reduced (RUN-2 and RUN-3) after conditioning at 400ºC for 20 minutes. As in the example here where the graphite ferrule is the cause of bleed, the baseline can be easily reduced by heating the column to 400ºC. Also since bleed from the septum at the injector can occur, do not lower the injector temperature

below 200ºC while performing column conditioning.

CAUTION When the injector temperature is lowered, the septum and O-ring get contracted leading to carrier gas leakage. If this is the case, recheck gas leakage before use.

STEP-6) Storing and reusing columns

Column performance can be deteriorated during storage by moisture or oxidation. It is best to plug both ends of column with supplied silicon rubber stoppers.

CAUTION When reusing a UA column, cut off 1 cm each of both ends of column after attaching column nut and graphite ferrule.

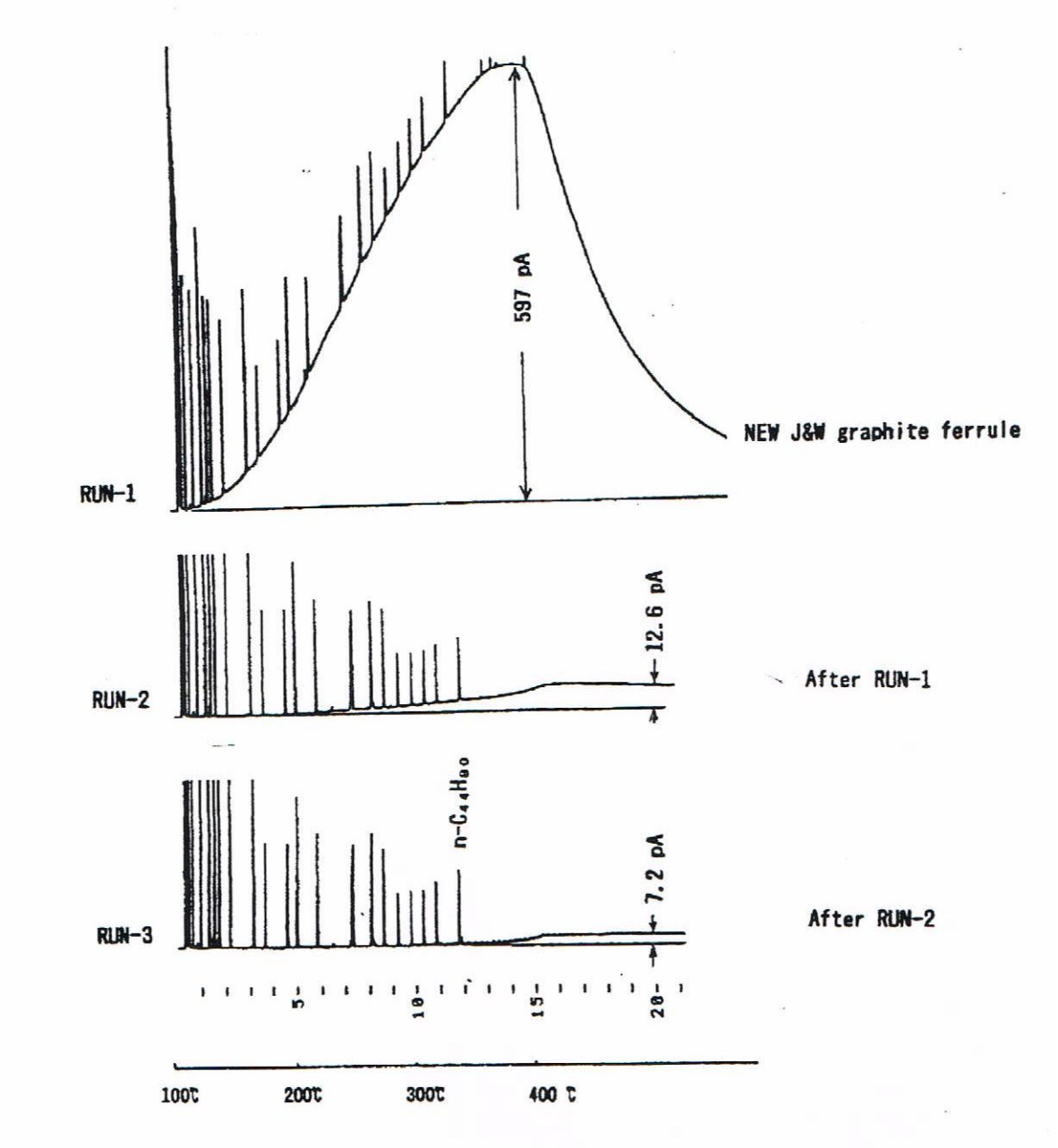

Fig. 1 Abnormally high baseline and its solution

Raised baseline due to bleed from graphite O-ring at detector joint is steadily reduced by repeated runs.

Analytical conditions :

Column: Ultra ALLOY-1 (HT), dimethyl polysiloxane , 5 m (0.25 mm id) , 0.15 µm film
Column Temp: 100ºC - 20 ºC /min - 400ºC, Injector temp.: 330ºC, Detector temp.: 400ºC
Carrier Gas: He 33 cm/sec, Split vent: 50 ml/min
Sample: C11 - C44, Test mixture (each at 500 ppm), 1 µL, split injection

2. Troubleshooting

2.1 High background at 300ºC or higher temperatures

(Columns: Ultra ALLOY$^+$-1, Ultra ALLOY$^+$-5, and Ultra ALLOY$^+$-17)

This trouble comes from GC and column. For GC, in addition to graphite ferrule which is used for connecting a column; septum at the injector, and Vespel ferrule in the FID adaptor that connects FID and column are the causes of high background level. If a Vespel ferrule is used as an FID adaptor packing, replace it with 1/4 inch stainless steel ferrule. To minimize a septum bleed, use high quality septa (Agilent septum, P/N 5181-1262) or increase the septum purge flow rate. To help determine the cause of bleed, compare the background of chromatograms obtained with programmed heating mode between when the injector is heated and not heated. In the case where the column has been contaminated by septum and injector, perform column conditioning described in STEP-5 in the preceding section then check the background level.

2.2 Contaminated columns

If the column is contaminated with high boiling oils, following the procedure below may revive the column. First, cut off 1 m of column at the column inlet. If this does not work, rinse the column with a solvent. (Caution: only methanol can be used for rinsing these columns: Ultra-ALOLOY-DX-30, -TRG, -65 and special columns) You can use commercial capillary column cleaner or simply clean the column by the method shown in Fig. 2. Remove the column from GC oven, then using an aspirator pull 2-3 mL of a solvent mixture (1:1 mixture of dichloromethane and methanol) through the column to clean the column.

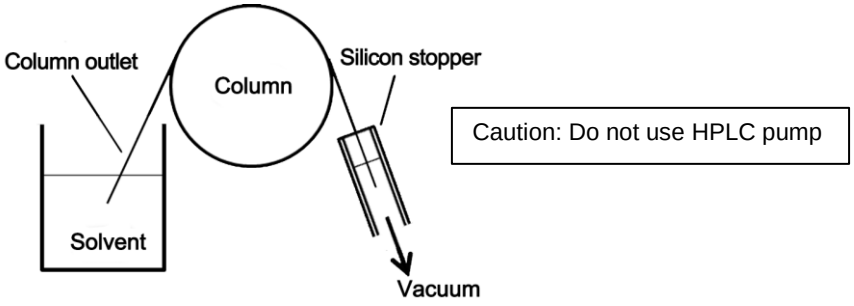

Fig. 2 Cleaning a column with solvent

Also, if contaminated materials can be derivatized, a silylating agent can be injected to the column at 250ºC, then perform a solvent cleaning. Injection of a large excess (hundreds of µL) of silylating agent forms a thick silicon film and deactivates active points; however, this will deteriorate the column separation performance greatly. Start out with injecting 5 µL of silylating agent. On the other hand, applying a silylating agent to a column of CW (polyethylene glycol) can greatly modify its functional groups; therefore, only solvent cleaning is recommended. After treatment mentioned above has been completed, allow the carrier gas to stream through the column for at least three hours at room temperature. Then install the column to GC, followed by heating it from room temperature to the max use temperature at ramp rate of 2-3ºC/min.

2.3 Decreased column resolution and peak tailing due to thinner liquid stationary phase at column inlet

Degraded column resolution and peak tailing are mainly caused by contamination at the column inlet, deteriorated liquid stationary phase at the column inlet, or thinned liquid phase at the column inlet/outlet due to prolonged exposure to high temperature of 350ºC or higher. As described in section 2.2 above, it may be necessary to cut off a length of column at the inlet or outlet of column, clean the column with a solvent or derivatize the liquid phase using a silylating agent. If the liquid phase at the column inlet seems to be thinned out, try cutting 1 m of column at the detector end, then install the column in reverse, i.e., the detector end to the injector. If this does not work, the column cannot be revived.

2.4 Peak tailing and broadening

A) Peak tailing and broadening caused due to injector structure

The column performance is greatly influenced by the structure of injector and detector. There are several injection methods such as Split, Splitless, On-column, and PTV. See GC manual or appropriate reference books for detail. Provided here is an example in which using UA columns by split injection method is described. The solvent tailing can often be a trouble in trace analysis, especially, splitter of own making or one made by part manufacturer is used. If the splitter is made of glass or metal and the part of it is exposed to the oven, the column nut temperature is much lower than injector temperature (in particular, the oven temperature is at near room temperature and the column nut is at 100ºC or below). This may cause a large peak tailing and greatly degrade the reproducibility and precision in quantitative analysis of high boiling compounds. Also, when a glass insert liner is used, contaminations and active spots of glass wool can be a problem in analysis of polar compounds and need to be deactivated. It is recommended that Frontier Labs specially deactivated insert (quartz insert for Agilent GC P/N: PY1-3361, for Shimadzu GC-17A and GC-2010 P/N: PYS-1741) should be used.

B) Peak tailing, broadening, abnormal signals caused due to detector structure

Depending on the detector internal structure, there may be absorption of polar compounds. When using FID detector with Shimadzu GC-17A or GC-2010, be sure to insert the column outlet into the detector until it hits the innermost end, then pull it out by 5 mm and tighten the nut. Abnormal signals may be observed if the column is not pulled out.

2.5 Using selective detector such as ECD, NP-FID(FTD), FPD, MASS(quadrupole), FT-IR

The column performance is significantly influenced depending on the degree of detector contamination. The Ultra ALLOY-1 series columns with film thickness of 0.15 µm or below offer extremely low bleed and can be used at 400ºC. It is recommended that the columns with film thickness of 0.5 µm or above be used at 300ºC or below. When using mass spectrometer or infrared spectrometer in which column is directly connected to the ion source or cell, temperatures of interface, ion source and cell are extremely important. Special attention should be paid when analyzing high boiling compounds. When a problem is encountered, using an FID detector is a good start for a solution., Many manufacturer recommend that Vespel ferrule containing 10% carbon be used for the ferrule used at the column outlet; however, leakage of carrier gas by thermal shocks or air leakage by vacuum can occur upon repeated thermal cycles. If there is such a leakage, use of Frontier Labs GC/MS adapter (P/N: MS604230) which uses 100% graphite ferrule (see Table 1 of this instruction manual) is recommended.

2.6 Using GC/MS (sector and ion-trap types)

(Using UA columns with Quadrupole GC/MS is basically the same as FS columns.)

In GC/MS analysis using a sector type mass spectrometer, a high voltage of several kV is applied on the ion source. There should be no problem when Frontier Labs connector kit (P/N: PY1-2210) in which the column outlet is connected to MS via a short FS column, or a jet separator is used. Never insert the outlet of a UA column directly to the ion source of MS. It must be at least 15 cm away from the ion source. In MS with the ion source applied voltage of over 8 kV, discharge may activate the safety system. For quadrupole mass spectrometer, the column can be directly connected to ion source. The rule of thumb for recommended max use temperature in GC/MS analysis is: 50ºC below the max use temperature for methyl silicon columns (UA^{+}-1, UA^{+}-5). In the case of ion-trap type GC/MS (Thermo Fisher and Hitachi), position the column end so that it is 5 mm away from the inlet of Vespel transfer line tip situated outside of the ion source.

2.7 Using at high temperatures (FID nozzle clogging)

When using a siloxane columns (Ultra ALLOY^{+}-1 or Ultra ALLOY^{+}-5) for a prolong period of time at 350ºC or higher temperatures, there may be depositions of decomposed liquid phase at the FID nozzle hole, making its diameter smaller than it should be. This makes it hard to ignite the FID. If this is the case, clean the nozzle hole.

2.8 Frequent spike noises

Spike noises originate from graphite ferrule flaking off from the column outlet. Replace old graphite ferrule with a new one when spike noises are observed on chromatogram.

2.9 Peak broadening of high boiling compounds, single compound splitting to two peaks, decreased peak height, or peak tailing

In the analysis of oligomers and oils, these problems are common. They originate from GC injector, column joints, and detector. See section 2.4 of this instruction manual. When cold spots exist in these locations, condensation of the target analytes occurs, resulting in abnormal peaks on chromatogram.

References

Instructions on capillary columns

1) R.R. Freeman sec. Ed."High Resolution Gas Chromatography" Hewlett-Packard

2) L.S. Ettre, "Introduction to Open Tubular Gas Chromatography" Perkin Elmer

3) C. Watanabe et al., "GC capillary column", Bunseki, No6, 1994, 441

Analytical problems associated with GC injection port and elution of high boiling compounds

1) C. Watanabe and Hashimoto, HRC&CC, 13 (1990) 610

2) C. Watanabe, Hashimoto and H. Tomita, HRC&CC, 5 (1982) 631

3) C. Watanabe et al. Japan Analytical Chemistry 38th annual meeting (1989) 1D02

4) C. Watanabe et al., HRC&CC, 5(1982) 630

5) K. Grob "Classical Split and Splitless Injection in Capillary GC" Huethig

Problems in using capillary columns with GC/MS

1) Watanabe, Hashimoto, Mass Analysis, 33 (1985) 183,

2) Watanabe, Hashimoto, Mass Analysis, 38 (1990) 65

Meatal capillary columns

1) C. Watanabe, R. Freeman, et al., "Basic performance of stainless steel capillary column (1)", Japan Chemical Society, 1991,1B03
2) C. Watanabe, R. Freeman, et al., "High temperature performance of stainless steel capillary column (2)", Japan Chemical Society, 1991,1B14
3) Morikawa et al., "Performance of metal capillary column", Japan Chemical Society, 1991, 1/02
4) Sato et al., "Polymer additive: Analysis of Irganox 1010", Japan Chemical Society, 1992, 1/03
5) Morikawa et al., "Investigation of metal capillary column for basic compounds", Japan Chemical Society, 1992, 1/03
6) Morikawa et al., "Investigation of metal capillary column for high temperature analysis", Japan Chemical Society, 1994, 2/08
7) Morikawa et al., "Investigation of large bore metal capillary column", Japan Chemical Society, 1993, 2/08