Trace Analysis of Volatile Organic Acids with the Agilent J&W DB-624UI GC Column

Application Note

Environmental

Authors

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Abstract

Agilent's new deactivation of the 6% cyanopropyl dimethylpolysiloxane (624) phase significantly improves acid performance and maintains very good performance for bases and alcohols. Similar phase selectivity makes it easy to replace existing columns.

Introduction

Volatile organic acids are organic compounds with acidic properties. The most common organic acids are the carboxylic acids, such as formic acid and acetic acid. Analysis of these acids has been problematic on traditional 624 phases due to reactivity within the cyanopropyl dimethylpolysiloxane phase. This resulted in loss of acidic compounds, no reproducible response, and retention times and bad peak shape that produced high detection limits. Luong *et al.* [1] compared different GC columns using a solventless stringent test mix and discovered very poor acid performance.

Response is influenced by conditioning time/temperature and is not stable after heating the column. After heating and conditioning the column at low temperature, acid recovery improves, but this effect is immediately lost once heat is applied again.

Agilent uses a new deactivation procedure for the 6% cyanopropyl dimethylpolysiloxane phase (624 phase). Using this deactivation procedure, acid performance is improved significantly, and the very good performance for bases and alcohols is maintained. The similar phase selectivity makes it easy for analysts to replace their current columns.

Agilent Technologies

Materials and Methods

There are 2 different Agilent 624 Ultra Inert stationary phases. In this application note, the Agilent J&W DB-624UI phase is described, but the results are also valid for Agilent J&W DB-Select 624UI for <467>. Conditions and supplies are shown with the individual analyses.

Results and Discusion

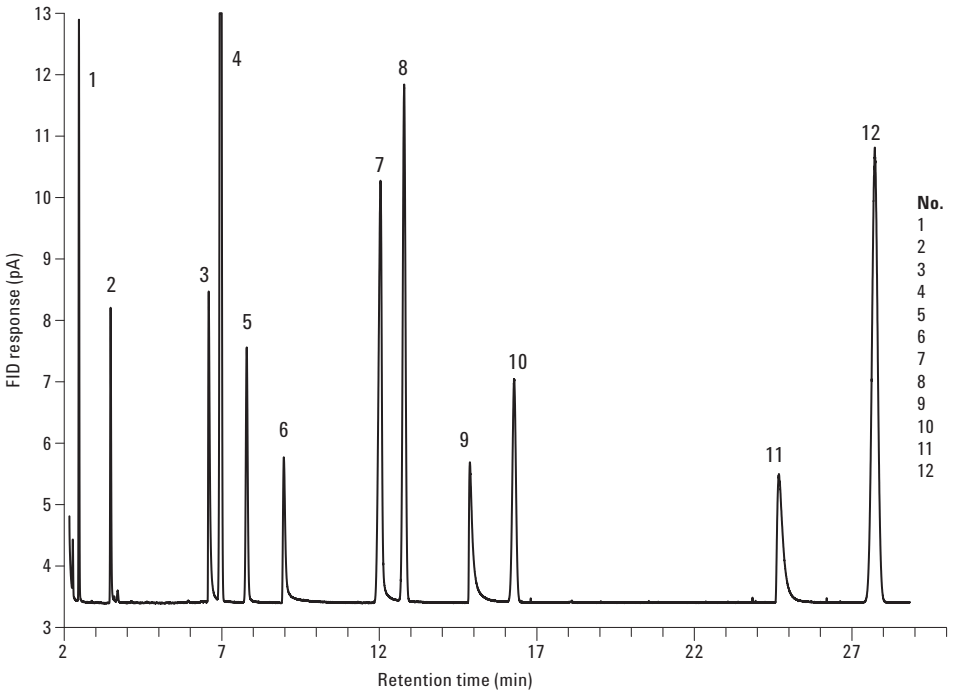
Ultra Inert testing

Agilent Ultra Inert columns are developed to deliver the best inertness for a wide range of active compounds.

To achieve this, every Ultra Inert column is tested using an Ultra Inert test mix. For the Agilent J&W DB-624UI column line, a new mix was developed that tests the inertness of the column at a low temperature with a good separation of all components (Figure 1).

Conditions

Column:	Agilent J&W DB-624UI, 30 m × 0.25 mm, 1.4 µm (p/n 122-1334UI)
Carrier:	Hydrogen, 42 cm/s
Oven:	70 °C isothermal
Inlet:	1 µL, split 1:116



No.	Compound	ng on-column
1	1-propanol	1
2	acetic acid	2
3	pyridine	1
4	n-octane	2
5	1-pentanol	4
6	1,2-propanediol	1
7	n-butyric acid	5
8	m-xylene	1
9	4-picoline	2
10	bromoform	25
11	dimethyl methylphosphonate	5
12	n-decane	4

Figure 1. Ultra Inert test mix for Agilent J&W 624UI columns tested after 1 hour at 260 °C and at ng levels, showing good acid performance for acetic acid at 2 ng and n-butyric acid at 5 ng.

Calibration curves

When a column is inert, linear calibration curves can be obtained. For example, Figure 2 shows 2 critical compounds on a 30 m × 0.32 mm × 1.8 µm column: n-butyric acid and 4-picoline. Curves show good linear response for acidic and basic compounds, even at low ng levels.

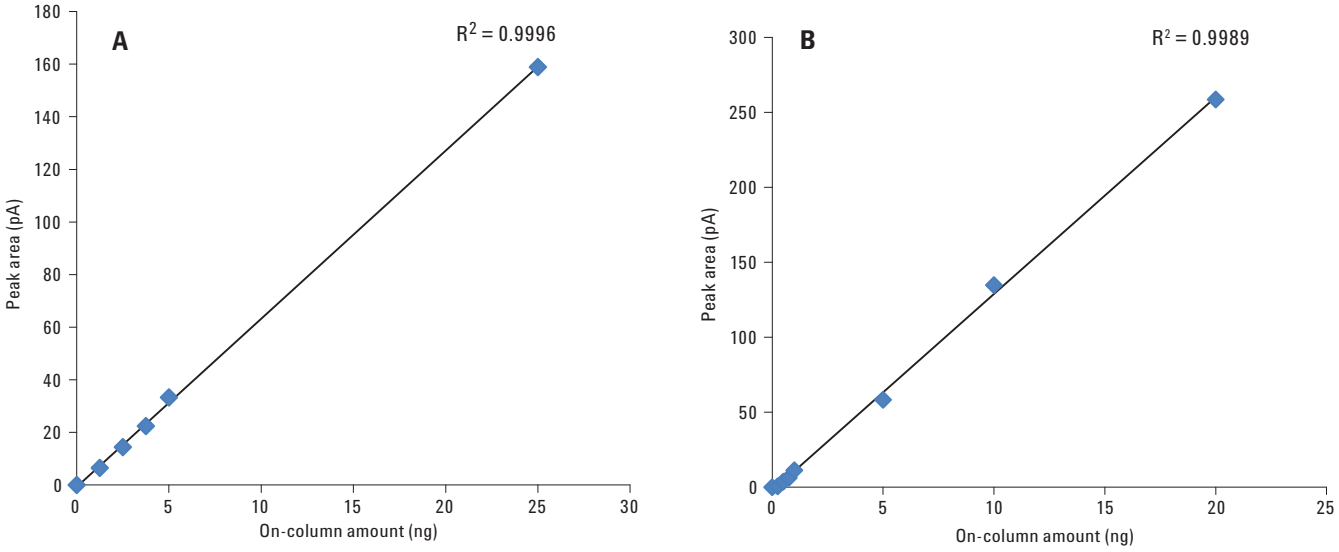
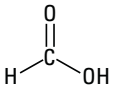
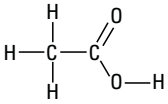
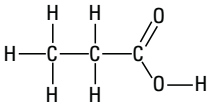
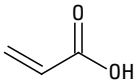
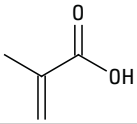
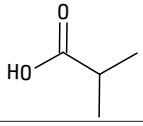
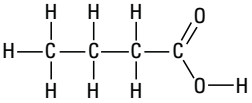


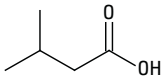
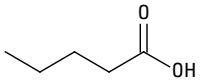
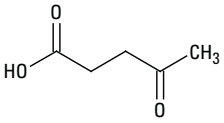
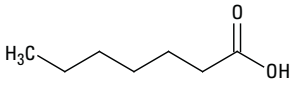
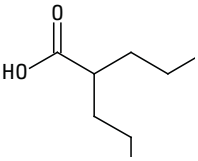
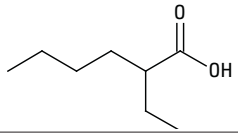
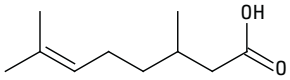
Figure 2. Calibration curves for (A) n-butyric acid and (B) 4-picoline on an Agilent J&W DB-624UI GC column.

Acid standards

Table 1 shows the range of organic acids used. Dilutions in dichloromethane were made to obtain the low on-column amount after split injection.

Table 1. Organic acids used in this work.

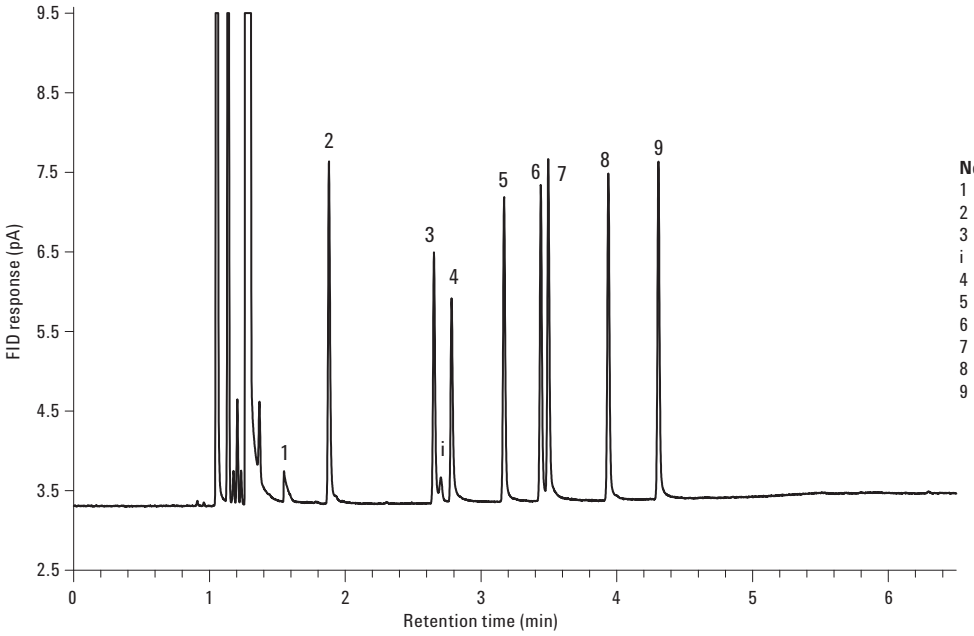
CAS	No. Carbons	Compound	Structure
64-18-6	C1	Formic acid	
64-19-7	C2	Acetic acid	
79-09-4	C3	Propionic acid	
79-10-7	C3	Acrylic acid	
79-41-4	C4	Methacrylic acid	
79-31-2	C4	Isobutyric acid	
107-92-6	C4	n-Butyric acid	

CAS	No. Carbons	Compound	Structure
503-74-2	C5	Isopentanoic acid	
109-52-4	C5	n-Pentanoic acid	
123-76-2	C5	Levulinic acid	
111-14-8	C7	n-Heptanoic acid	
99-66-1	C8	2-Propyl pentanoic acid	
149-57-5	C8	2-Ethyl hexanoic acid	
502-47-6	C10	Citronellic acid	

A narrow bore DB-624UI GC column was installed in an Agilent 7890A GC with FID. After conditioning, a C_1-C_5 organic acid test mix (0.5-1 ng) was injected (Figure 3). Because the response for formic acid on an FID is very low, a high concentration (250 ng) of this compound was added to obtain a peak. However, this has a negative influence on its peak shape.

Conditions

Column:	Agilent J&W DB-624UI, 30 m × 0.25 mm, 1.4 µm (p/n 122-1334UI)
Carrier:	Hydrogen, 3 mL/min constant flow
Oven:	70 °C (1 min), then 20 °C/min to 160 °C
Inlet:	250 °C, 1 µL, split 1:200
Inlet liner:	4 mm, glass wool (p/n 5183-4647)
FID:	260 °C



No.	Compound	[ng]
1	Formic acid	250
2	Acetic acid	1.0
3	Propionic acid	0.5
i	impurity	
4	Acrylic acid	0.5
5	Isobutyric acid	0.5
6	n-Butyric acid	0.5
7	Methacrylic acid	0.5
8	Isopentanoic acid	0.5
9	n-Pentanoic acid	0.5

Figure 3. Organic acid mix C1-C5 on an Agilent J&W DB-624UI GC column.

To demonstrate reproducibility, the injection was repeated 6 times (Figure 4). Retention time and responses were stable. For conditions, see Figure 3.

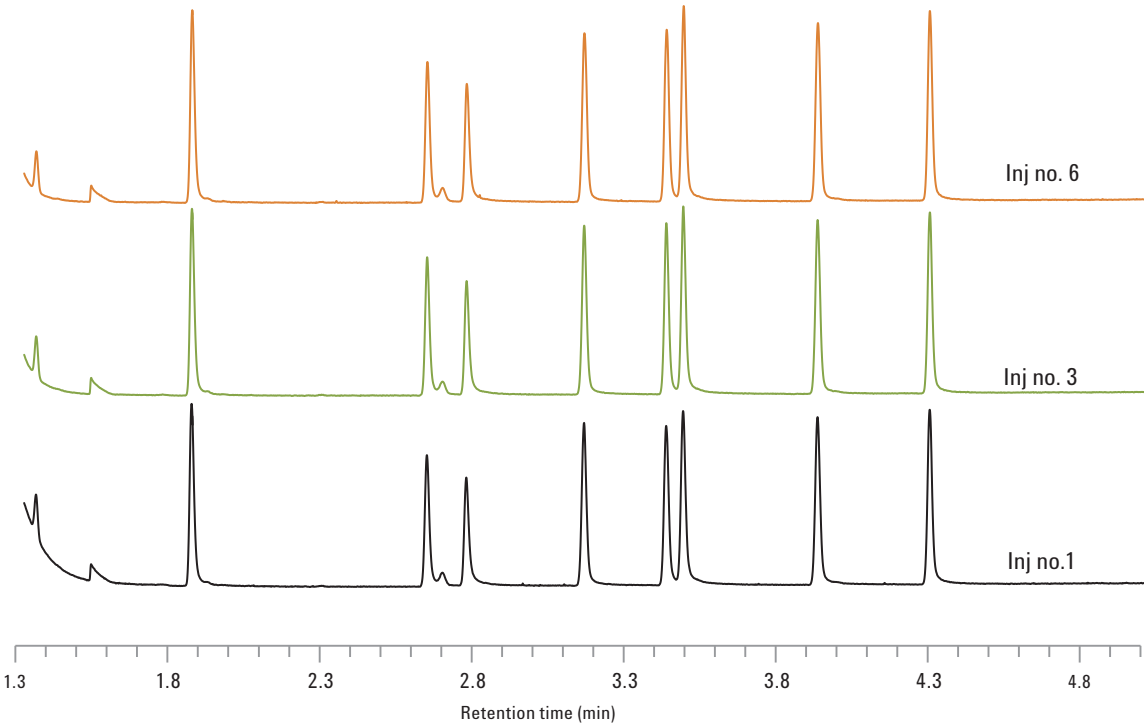


Figure 4. Organic acid mix C1-C5 on an Agilent J&W DB-624UI GC column after 6 injections.

A test mix with C1-C8 organic acid was prepared and injected on GC-FID (Figure 5). With this test mix, a low level amount of formic acid was used, which was below the FID detection limit. Higher molecular weight acids at 0.6 ng and 6 ng showed good peak shape.

Conditions

Column:	Agilent J&W DB-624UI, 30 m × 0.25 mm, 1.4 µm (p/n 122-1334UI)
Carrier:	Hydrogen, 3 mL/min constant flow
Oven:	70 °C (1 min), then 20 °C/min to 260 °C
Inlet:	250 °C, 1 µL and 0.1 µL, split 1:200
Inlet liner:	4 mm, glass wool (p/n 5183-4647)
FID:	260 °C

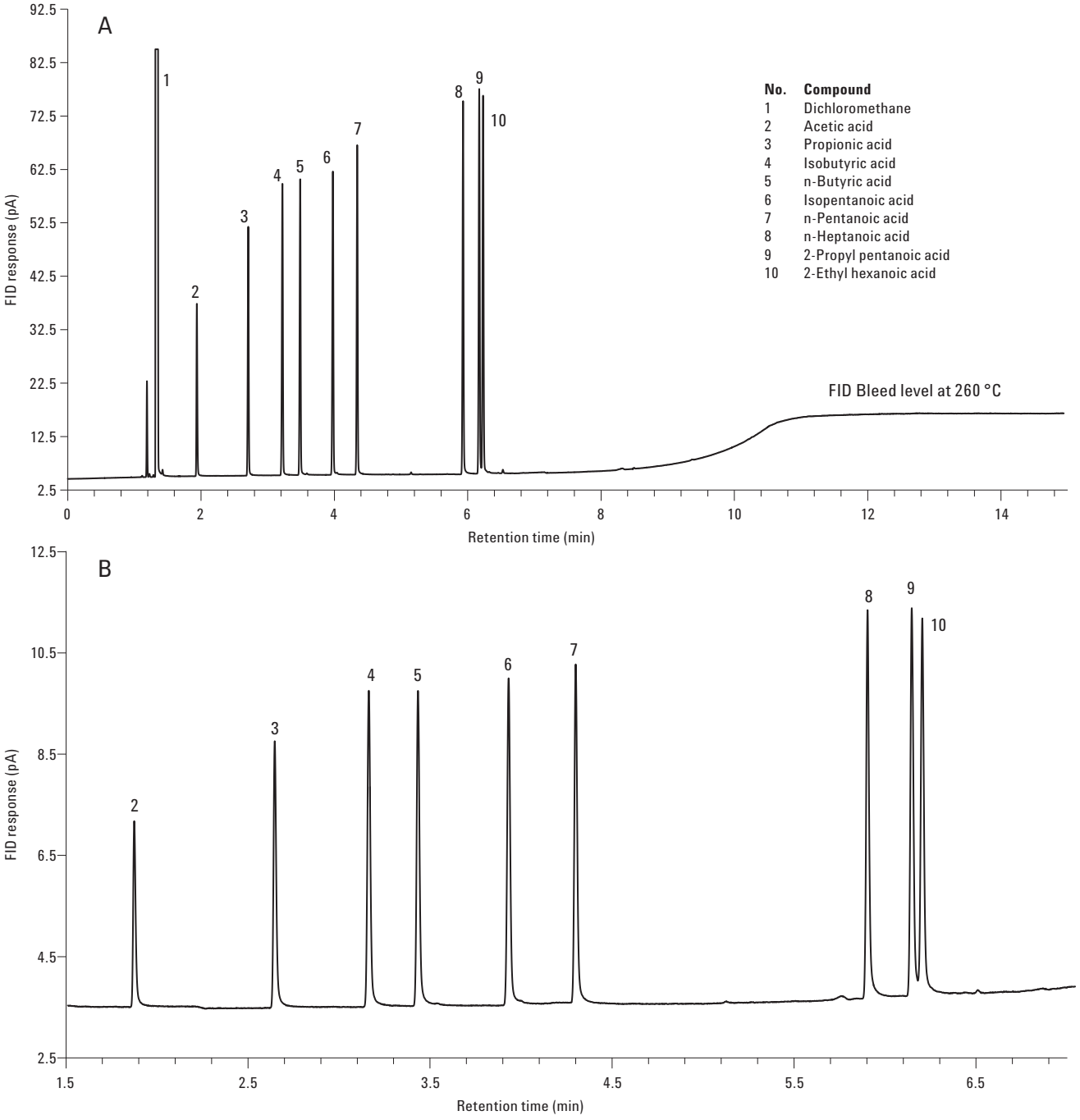
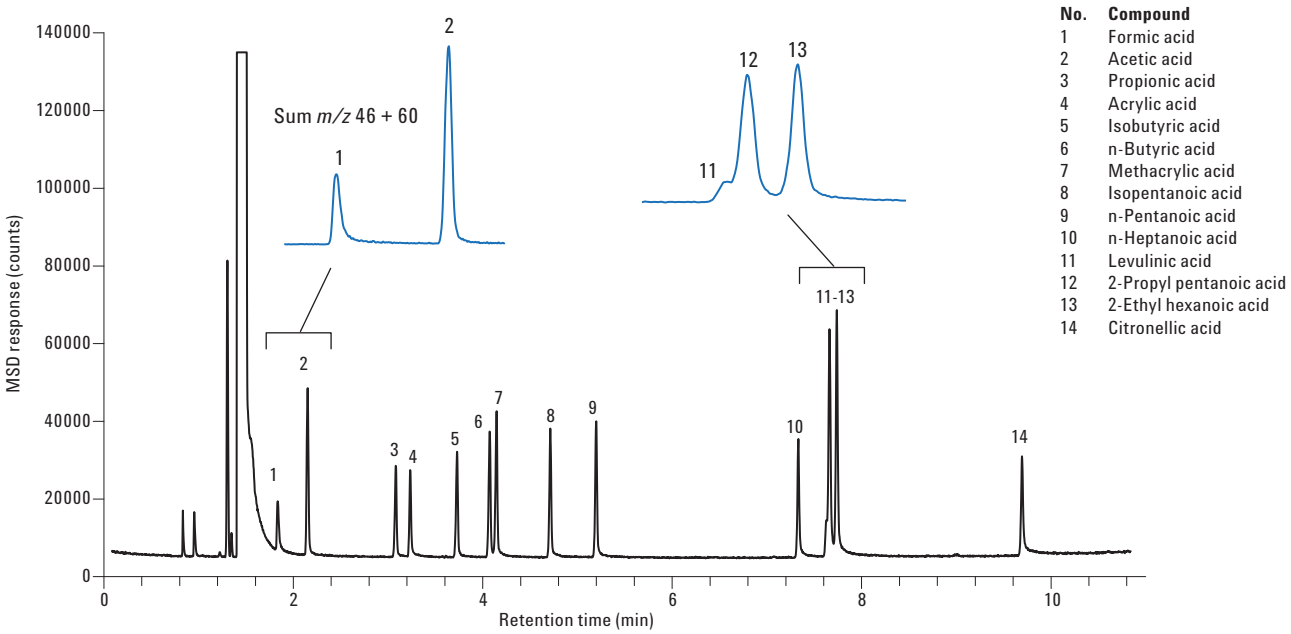


Figure 5. Organic acid mix C1-C8 on an Agilent J&W DB-624UI GC column at (A) 6 ng and (B) 0.6 ng.

Because formic acid analysis using FID is not a method of choice, MSD was also used for detection. A new mix was prepared. Formic acid was injected at 17 ng on-column, as well as some higher organic acids (Figure 6). Using MSD, good analysis of organic acids was possible, even for formic and citronellic acids.

Conditions

Column:	Agilent J&W DB-624UI, 30 m × 0.25 mm, 1.4 µm (p/n 122-1334UI)
Carrier:	Helium, 3 mL/min constant flow
Oven:	70 °C (1 min), then 20 °C/min to 260 °C
Inlet:	250 °C, 1 µL, split 1:20
Inlet liner:	4 mm, glass wool (p/n 5183-4647)
Agilent 5973 MSD:	Transfer 250 °C, EI source 230 °C, Quad 150 °C, EI full scan *m/z* 10-550



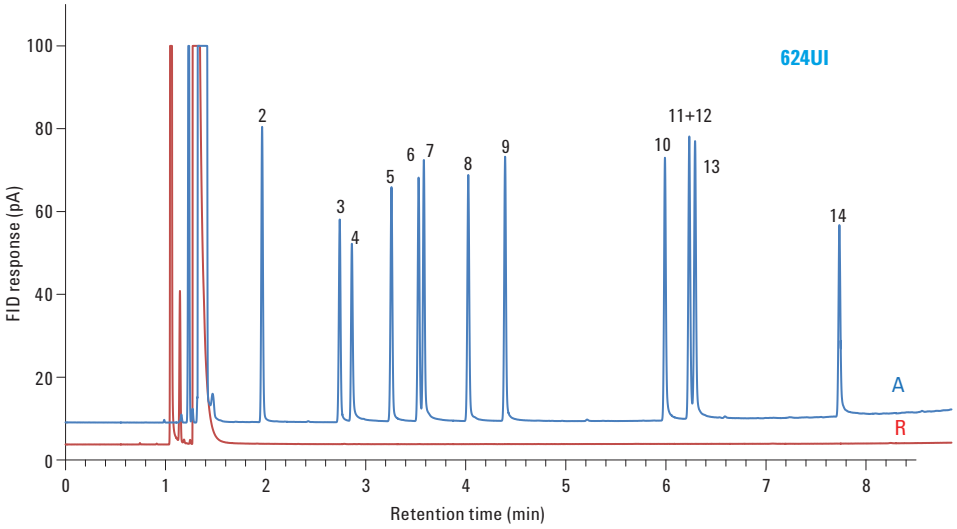
No.	Compound
1	Formic acid
2	Acetic acid
3	Propionic acid
4	Acrylic acid
5	Isobutyric acid
6	n-Butyric acid
7	Methacrylic acid
8	Isopentanoic acid
9	n-Pentanoic acid
10	n-Heptanoic acid
11	Levulinic acid
12	2-Propyl pentanoic acid
13	2-Ethyl hexanoic acid
14	Citronellic acid

Figure 6. Organic acid mix C1-C10 (6 to 17 ng) on an Agilent J&W DB-624UI GC column.

Comparing 0.32 mm id columns

As well as 0.25 mm id columns, those of 0.32 mm id are also widely used. Using GC-FID, the C_1-C_{10} organic acid mixture was tested on a 0.32 mm id column and compared to a non-Agilent 624 phase with the same dimensions. The columns were tested at the same time and in the same GC (2 channels) after conditioning for 1 hour at 260 °C. As expected, formic acid was below the detection limit, and levulinic acid was not separated from 2-propyl pentanoic acid (fewer plates compared to a 0.25 mm id column). However, other acids showed good elution from the DB-624UI column (Figure 7). No acids were detected on the traditional phase in the non-Agilent column.

Columns:	Agilent J&W DB-624UI, 30 m × 0.32 mm, 1.8 µm (p/n 123-1334UI) Non-Agilent 624. 30 m x 0.32 mm, 1.8 µm
Carrier:	Hydrogen, 4 mL/min constant flow
Oven:	70 °C (1 min), then 20 °C/min to 260 °C
Inlet:	250 °C, 1 µL, split 1:200
Inlet liner:	4 mm, glass wool (p/n 5183-4647)
FID:	260 °C



No.	Compound
1	Formic acid (< DL)
2	Acetic acid
3	Propionic acid
4	Acrylic acid
5	Isobutyric acid
6	n-Butyric acid
7	Methacrylic acid
8	Isopentanoic acid
9	n-Pentanoic acid
10	n-Heptanoic acid
11	Levulinic acid
12	2-Propyl pentanoic acid
13	2-Ethyl hexanoic acid
14	Citronellic acid

Figure 7. Organic acid mix C_1-C_{10} (6 to 17 ng) on an Agilent J&W DB-624UI column (blue) and a traditional non-Agilent 624 column (red) after conditioning at 260 °C for 1 hour.

Conclusions

Agilent J&W DB-624UI and Agilent J&W DB-Select 624UI for <467> GC columns are well suited for the analysis of the most stringent components, including C_1-C_{10} organic acids. These DB-624UI columns represent a major breakthrough in inertness compared to traditional 624 phases. Quality is controlled using an Ultra Inert test mix, which guarantees column-to-column inertness for the most stringent probes.

False negatives or incorrect values for acidic compounds were avoided. Selectivity remained similar compared to current Agilent columns, requiring minimal revalidation for chemists who want to replace their traditional 624 column with the latest Agilent J&W DB-624UI column. In addition, custom-made dimensions are possible.

Reference

1. J. Luong, R. Gras, W. Jennings. *J. Sep. Sci.* 30, 2480 (2007).

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