Agilent J&W DB-624 UI Ultra Inert GC Capillary Column for Challenging Industrial Applications

Application Note

Environmental and Industrial Chemicals

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Abstract

A novel stationary phase for use with gas chromatography has been recently innovated. The new stationary phase has a composition of 6% cyanopropyl phenyl and 94% polydimethylsiloxane, and is commercialized as the Agilent J&W DB-624 UI Ultra Inert GC Column.

In addition to traditional applications performed by the classical 624 type stationary phase, the DB-624 UI was found suitable for use in a number of difficult and challenging chromatographic applications that are atypical for this stationary phase. Demonstrated are the characterization of oxygenated compounds in wastewater, phenol, and alkylated phenols used as anti-oxidant in fuels and lubricants, furans analysis for cellulose degradation monitoring, and sulfur compounds in hydrocarbons, to name a few.

The stationary phase demonstrated a high degree of inertness with low bleed characteristics with a maximum operating temperature of up to 260 °C and a selectivity that is similar to the traditional 624 phase. The column is available in different dimensions and was found to be compatible with different GC techniques such as single or multi-dimensional gas chromatography, comprehensive two-dimensional gas chromatography, and hyphenated techniques such as GC/MS.

Agilent Technologies

Introduction

Capillary column technology contributes substantially to the development of high resolution gas chromatography with desired attributes such as high chromatographic efficiency, resolution, and performance reliability [1-3].

Recent advances in deactivation techniques and effective coating technologies resulted in the commercialization of a new and improved generation of 624 type stationary phases with low bleed with a high degree of inertness. First introduced in 1986, the 624 type column stationary phase is comprised of 6% cyanopropyl phenyl and 94% polydimethylsiloxane polymer [4].

As a stationary phase, this polymer and the specific phase ratio for the DB-624 wall coated open tubular (WCOT) column was designed particularly for volatile organic analysis (USEPA-624) [5]. Since then, it has been found to be useful in a number of difficult chromatographic applications. Constraints encountered include column longevity, compatibility with an electron capture detector, reactivity with active acidic and basic compounds, and a limited maximum operating temperature. The poor response to these active GC solutes was a point of concern where cyanopropyl phenyl stationary phases where shown to have varied degrees of activity when the columns were subjected to elevated temperatures and a more stringent set of column performance test conditions were employed [6].

In this article, in addition to the traditional applications suitable for use with 624 type stationary phases reported earlier in the literature [4,5], applications of industrial significance are illustrated and column performance is reported.

Experimental

An Agilent 6890N Network Gas Chromatograph, equipped with an Agilent G-4512A autosampler, two split/splitless inlets, and a flame ionization detector (FID) was employed for the applications of furans in transformer oil, phenols and alkylated phenols, and sulfur containing compounds.

An Agilent 7890A Plus Gas Chromatograph equipped with an Agilent 7697A Headspace Sampler and a 111 vial autosampler were also used for the characterization of volatile oxygenated compounds. This system was equipped with two split/splitless inlets and a FID. The headspace oven temperature was 80 °C, the loop temperature and transfer line temperature were 150 °C, and vial equilibrium time was 5 min. Pressurization time was 0.1 min, vial fill pressure was 15 psig, vial flow was 50 mL/min, and injection time was 0.6 min. A 5 mL sample was added to 20 mL headspace vials, and the injection loop size was 1 mL.

For all applications, the temperature, unless otherwise stated, was programmed from 40 °C (2 min) to 250 °C at 15 °C/min, and maintained at 250 °C for 10 min. The FID temperature was at 250 °C with hydrogen flow rate at 30 mL/min, air flow rate at 350 mL/min, and nitrogen flow rate at 30 mL/min. Chromatographic data obtained with ChemStation B.03.02.

Apart from the furans in transformer oil application, carrier gas was helium with an average linear velocity of 40 cm/s. In the furans in transformer oil application, the instrument was also equipped with a 3-port capillary flow technology flow plate for backflushing purposes. Midpoint pressure was delivered by connecting a 0.5 m × 0.25 mm uncoated, but deactivated fused silica capillary tubing from the second split/splitless inlet to the planar microfluidic device. The gas chromatograph conditions used are as follows: an Agilent J&W DB-624 UI, 2 m × 0.32 mm, 1.8 µm was used in the first section and a DB-624UI, 10 m × 0.32 mm, 1.8 µm was used in the second section. These two columns were cut from a single DB-624 UI, 60 m × 0.32 mm, 1.8 µm column, which had a stationary phase comprised of 6% cyanopropyl phenyl and 94% polydimethylsiloxane. The column flow in the column ensemble was 6.6 mL/min helium, in constant flow mode. The inlet pressure was 12.6 psig at 40 °C, while the auxiliary pressure was 10.0 psig at 40 °C to deliver the flows required. During the backflush state, the inlet pressure was lowered to 2 psig final pressure at a rate of 99 psig/min while the mid-point pressure was raised to 17 psig at a rate of 99 psig/min.

The inlet temperature was 250 °C, operating in split mode at a ratio of 3:1 and equipped with an Ultra-inert liner (p/n 5190-2294) and the injection size was 1 µL for the liquid injection, and 1 mL for the headspace injection.

Various DB-624UI columns were employed including:

- 60 m × 0.32 mm, 1.8 µm
- 30 m × 0.25 mm, 1.4 µm
- 20 m × 0.18 mm, 1.0 µm
- 2 m × 0.32 mm, 1.8 µm used as a guard column coupled to a 10 m × 0.32 mm, 1.8 µm, cut from a 60 m × 0.32 mm, 1.8 µm.

Chemicals and solvents used for testing were obtained from Sigma-Aldrich.

Results and Discussions

A 12-component probe mixture was used to assess the new stationary phase inertness. Figure 1 shows a chromatogram obtained with an on-column amount of 1 ng of 1-propanol, 2 ng of acetic acid, 1 ng of pyridine, 2 ng of *n*-octane, 4 ng of pentanol, 1 ng of 1,2-propanediol, 5 ng of *n*-butyric acid, 1 ng of *m*-xylene, 2 ng of picoline, 25 ng of bromoform, 5 ng of dimethyl methyl phosphonate, and 4 ng of *n*-decane. Respectable peak symmetry and response were obtained for acidic compounds such as acetic acid and *n*-butyric acid, for basic compounds such as pyridine and picoline, as well as other active components such as 1,2-propanediol and dimethyl phosphonate. The performance of the new stationary phase indicates that the lack of inertness and stability of the previous generation of cyanopropyl-phenyl stationary phase have been successfully addressed. This in turn can broaden the potential application of this column technology to industrial analyses where there has been an unmet need for an inert, stable mid-polarity selectivity column [7].

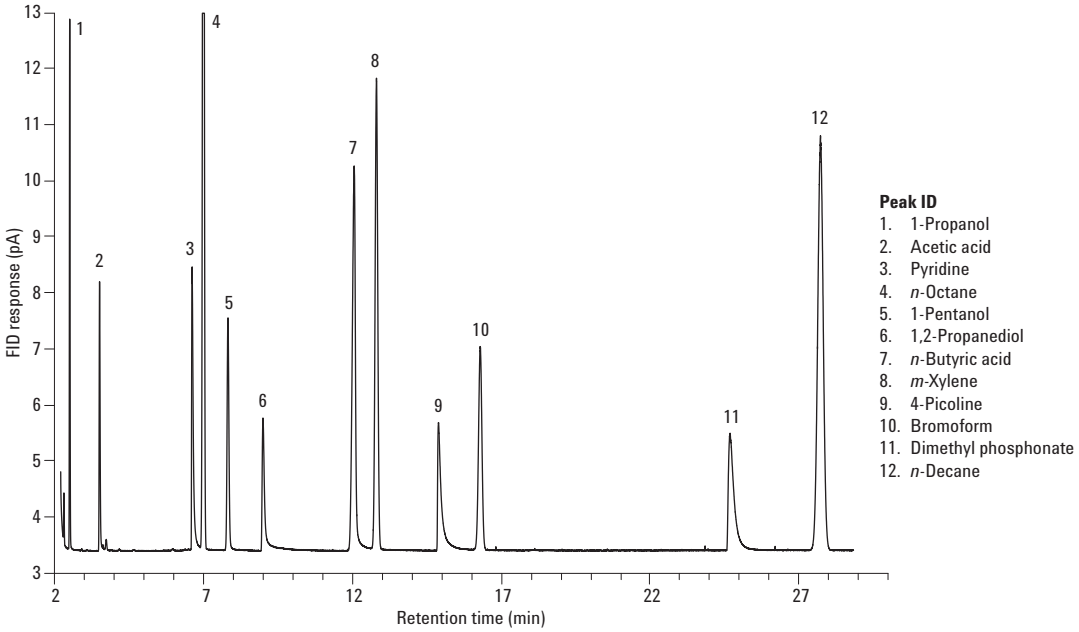

Figure 1. Twelve-component probe mixture at 70 °C isothermal.

Application:
Oxygenated compounds in wastewater

Common oxygenated industrial chemicals are monitored in trace levels in waste or process water. The DB-624 UI showed respectable separation capabilities and excellent peak efficiencies, as illustrated in Figure 2. Samples were analyzed by HS/GC/FID using an Agilent J&W DB-624 UI 60 m × 0.32 mm, 1.8 µm column with conditions stated in the experimental section. The concentrations of the analytes of interest were at 100 ppm (w/w) in water.

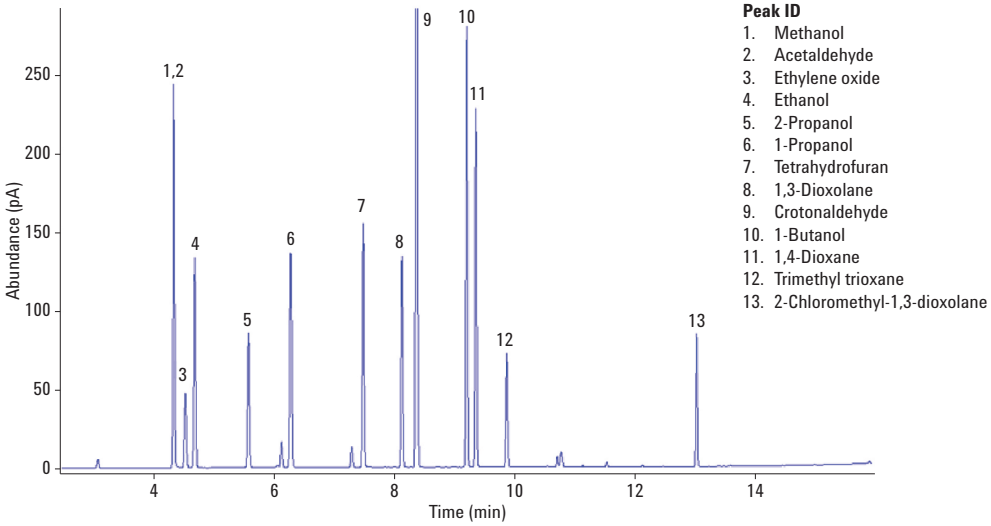

Figure 2. Oxygenated compounds in waste water.

Application:
Analysis of phenols and alkylated phenols in fuels and lubricants

The production of phenols commenced in the 1860s and has proven to be very useful in many applications from plastics to agricultural chemicals. Figure 3 shows an overlay of five chromatograms of 100 ppm (w/w) each of popular phenolic compounds in cyclohexane. These phenolic compounds are often encountered in various industrial segments such as pulp-and-paper, dyes, and textiles. The samples were analyzed by GC/FID using an Agilent J&W DB-624UI 20 m × 0.18 mm, 1.0 µm column.

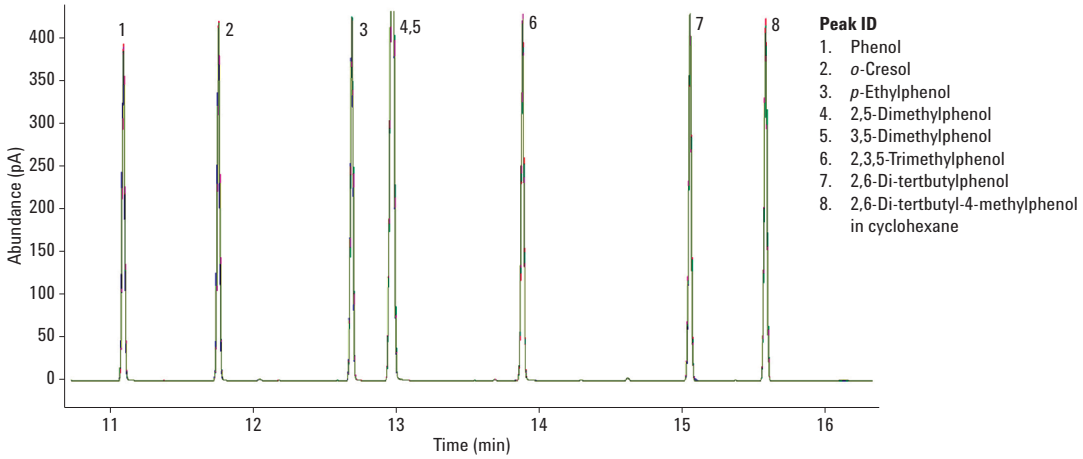

Figure 3. Analysis of phenols and alkylated phenols in fuels and lubricants.

Application: Furans analysis for cellulose degradation monitoring

Furans are a group of toxic chemicals that can be produced from chemical processes such as chlorine bleaching in the paper production, the combustion process, or by cellulous degradation. Trace levels can be found ubiquitously in the environment. An interesting fact is that furans were also found in off-grade Manuka honey produced by European bees used for medicinal purposes [8]. The inertness of this phase for this class of molecules provided an option to their chromatographic separation. Figure 4 shows an overlay of chromatograms of 10 ppm (w/w) of furfural, furfuryl alcohol, 2-furmethyl ketone, 5-methyl furfural, and 5-hydroxymethyl furaldehyde in methanol using an Agilent J&W DB-624 UI, 2 m × 0.32 mm, 1.8 µm column employed as a guard column coupled to a DB-624 UI, 10 m × 0.32 mm, 1.8 µm cut from a DB-624 UI, 60 m × 0.32 mm, 1.8 µm column.

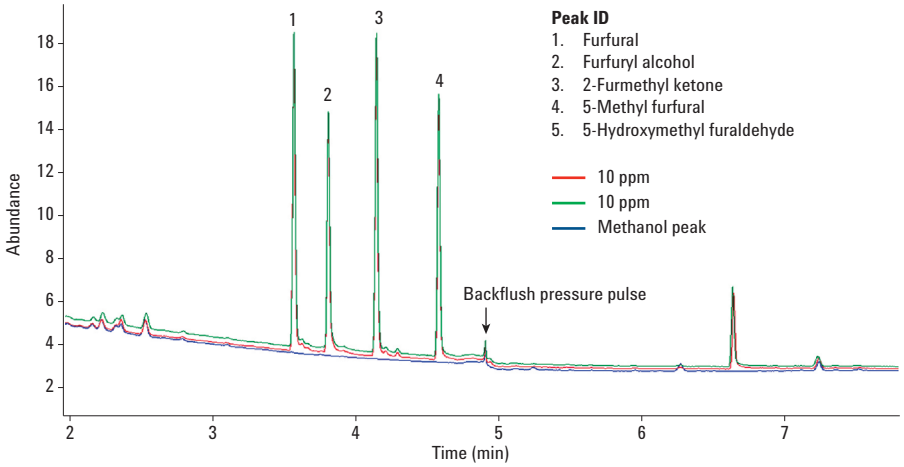

Figure 4. Furans analysis for cellulose degradation monitoring.

Application:
Common sulfur containing compounds in hydrocarbons

A challenging chromatographic application is the analysis of sulfur containing molecules due to their reactivity and adsorption to active surfaces. This new stationary phase showed a high degree of inertness, even with volatile molecules such as methyl and ethyl mercapatans, as shown in Figure 5. Samples were analyzed by GC/FID using an Agilent J&W DB-624 UI, 60 m × 0.32 mm, 1.8 µm column.

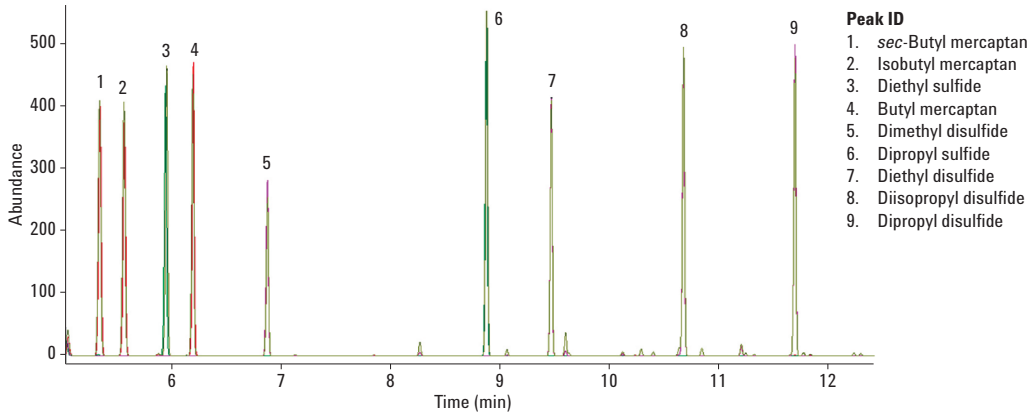

Figure 5. Sulfur-containing compounds in hydrocarbons.

Conclusions

In addition to traditional applications performed by the 624 type stationary phase, the Agilent J&W DB-624 UI, a newly commercialized capillary column, was found suitable for use in a number of industrially significant applications such as the determination of phenol and alkylated phenols used as anti-oxidants in fuels and lubricants, oxygenated compounds in wastewater, sulfur compounds in hydrocarbons, and furans in transformer oils. The stationary phase demonstrated a high degree of inertness with a low bleed characteristic, and a unique selectivity. The column is available in different dimensions, and was found to be compatible with contemporary techniques such as GC/GC, GC×GC, and GC/MS.

Acknowledgements

Credit must be given to Dr. Taylor Hayward for his assistance in making the chlorinated phenols, furan standards, and insight on transformer oil analysis. Agilent Technologies Chemistry Team, Dr. Mitch Hastings, Dr. Janice Perez of Agilent were acknowledged for the fruitful and stimulating discussions on column deactivation technologies. Dr. Martine Stolk, Dow Global GC Steering Team were acknowledged for their support and encouragement.

The project is partially funded by Dow Analytical Technology Center's 2013 Technology and Renewal and Development Funds.

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Printed in the USA
November 4, 2014
5991-5197EN

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