Industrial Applications with a New Polyethylene Glycol-Based GC Column

Application Note

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Abstract

The increasing need for sensitive, reproducible, and reliable analysis of active analytes is placing demands on GC column technology. These analyses are challenging due to potential adsorption of analytes to the active sites in the GC flowpath. Agilent Technologies has recently produced an Agilent J&W DB-WAX Ultra Inert GC column. This highly inert capillary column is coated with an innovative new polyethylene glycol (PEG) stationary phase. This application note demonstrates the excellent inertness performance of this stationary phase in the analysis of compounds with polar functional groups. The column was found to be suitable for many challenging industrial applications.

Introduction

In gas chromatography, the column is the heart of the system where separation of sample components takes place through interactions between analytes and the stationary phase. GC columns with polyethylene glycol (PEG) stationary phase are widely used for analyzing compounds with polar functional groups. PEG phase demonstrates a unique separation mechanism based on hydrogen bonding, and acid-base interaction, making it suitable for many industrial applications. It is also a good option for offering phase orthogonality in techniques such as GC-GC or GC×GC. However, PEG-based columns are less stable, less robust, and have a lower maximum operating temperature when compared to most polysiloxane-based columns. They exhibit shorter lifetimes, and are more susceptible to damage upon overheating or exposure to oxygen.

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Traditional PEG columns have constraints particularly with active polar compounds such as alcohols, aldehydes, and organic acids due to a lack of overall stationary phase inertness [1]. These molecules can either adsorb or absorb onto active sites in the stationary phase, resulting in lower responses and tailing peaks, which can compromise system reliability and performance.

Recent advances in surface deactivation techniques and high efficiency static coating technologies led to the development, commercialization, and implementation of an improved generation of PEG columns. These columns include the Agilent J&W DB-WAX Ultra Inert GC column, which has a high degree of inertness [1-4].

This application note evaluates the Agilent DB-WAX Ultra Inert column in terms of efficiency, reactivity, and overall inertness against various, challenging industrial applications. Testing the columns using demanding test probes containing problematic compounds including alcohols, aldehydes, and organic acids, proved the high inertness performance of the column.

Experimental

Instrumentation

An Agilent 7890A+ network GC, equipped with an Agilent 7693 autosampler, two split/splitless inlets, and a flame ionization detector was used in this study. Table 1 summarizes the instruments and conditions. Chromatographic data were obtained with Agilent ChemStation software version B.04.03.SP.

Table 1. GC conditions.

Parameter	Value
GC System:	Agilent 7890A+/FID
Column:	Agilent J&W DB-WAX Ultra Inert, 20 m × 0.18 mm, 0.3 µm (p/n 121-7023UI)
Autosampler:	Agilent 7693, 1.0 µL injection volume
Carrier gas:	Hydrogen, constant flow mode, 28 cm/sec
Inlet:	Split/splitless, 250 °C, split ratio 25:1, equipped with an Agilent Ultra Inert inlet liner (p/n 5190–2294)
Oven:	40 °C (1 minute) to 250 °C at 20 °C/min
FID	250 °C, H_2 30 mL/min, air 350 mL/min, N_2 30 mL/min (constant column + make up flow)

Samples, chemicals, and reagents

Three test mixes: a DRO/ORO range calibration standard, a polar ISO test mix, and a Grob test mix were obtained from Restek Corporation (Bellefonte, Pennsylvania). An eight-component phenol mix was prepared in cyclohexane. Chlorinated hydrocarbons in process water were extracted 1:1 with cyclohexane using a piston-extraction device [5]. Butyl phenyl ether, dimethoxybenzene, and trimethoxybenzene were prepared at a concentration of 100 µg/mL in hexane. Chemicals and solvents used for standard and sample preparation were obtained from Sigma-Aldrich.

Results and Discussion

Test methods and standards

To evaluate the overall performance of the new stationary phase, three test mixes were analyzed.

- **A 12 component DRO/ORO range calibration standard:** A 12 component DRO/ORO range calibration standard, with carbon numbers from C10 to C32, was analyzed on a DB-WAX Ultra Inert column to assess the hydrocarbon range. The chromatogram in Figure 1 shows that all hydrocarbon compounds eluted with sharp symmetrical peaks.

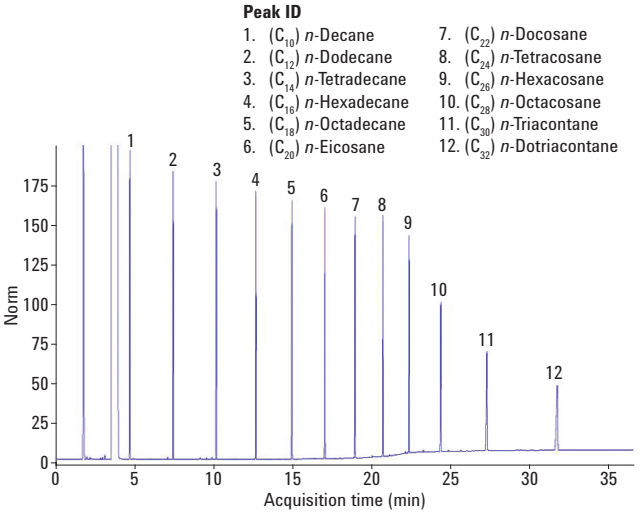

Figure 1. Analysis of a hydrocarbon mix, with carbon numbers from C10 to C32, separated using an Agilent J&W DB-WAX Ultra Inert GC column.

- **A polar ISO column test mix:** A polar ISO column test mix was used for detection of column activity. This mix contained representative compounds with different polar functional groups including aniline, chlorophenol, alcohol, ester, and ketone with long hydrocarbon chains. Figure 2 shows the symmetrical peak shapes for all the active components, including the basic compound aniline (Peak 3), indicating the high level of inertness of the DB-WAX Ultra Inert column.

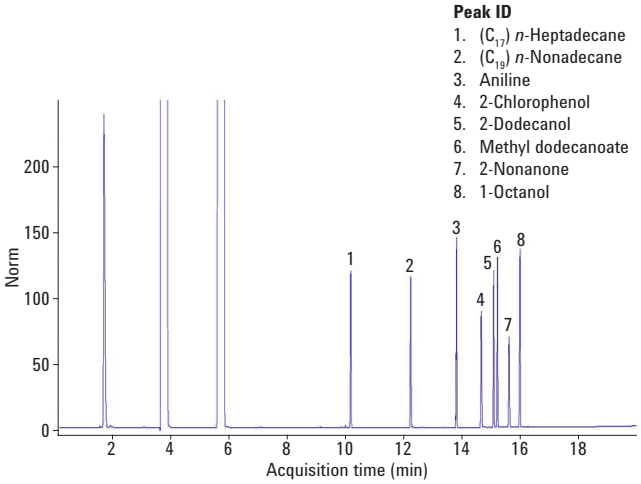

Figure 2. Analysis of a polar ISO test mix separated using an Agilent J&W DB-WAX Ultra Inert GC column.

- **A Grob test mix (12 components):** In addition to the polar ISO column test mix, a more demanding test mix, a Grob mix, was analyzed for extra assessment of the inertness performance of the DB-WAX Ultra Inert column. This mix contained more challenging test probes such as 2,3-butanediol, dicyclohexylamine, and 2-ethylhexanoic acid. The new column showed excellent separation capabilities and peak efficiencies, as illustrated in Figure 3. Compounds such as dicyclohexylamine, 2,3-butanediol, and 2-ethylhexanoic acid can have less than ideal chromatographic performance, as reported in the literature. Figure 3 shows that these active components exhibited excellent peak symmetry with the DB-WAX Ultra Inert column.

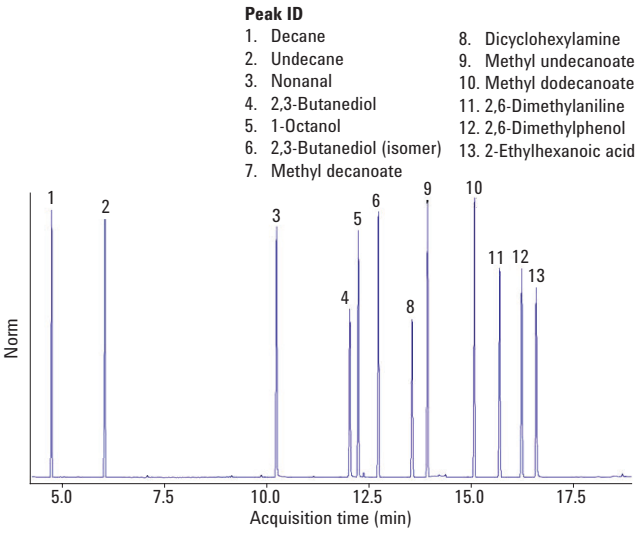

Figure 3. GC/FID chromatogram of a Grob test mix separated using an Agilent J&W DB-WAX Ultra Inert GC column.

Hydrolysis and swelling studies

Some traditional PEG stationary phases can become unstable with aqueous injection, leading to column degradation, reduced lifetime, and poor reproducibility. To evaluate the performance of the DB-WAX Ultra Inert column for aqueous injection, the polar ISO test mix was analyzed repeatedly with 30 water injections (1 µL) between sample injections. The results showed no retention time stability drift resulting from repeated injections of water. Separation and peak shape were also maintained over the course of 150 injections of water (Figure 4). The DB-WAX Ultra Inert column demonstrated excellent inertness and phase stability for aqueous injections. The high tolerance towards water allows the direct injection of aqueous samples, which offers the benefit of rapid analysis without the need of tedious sample pretreatment procedures.

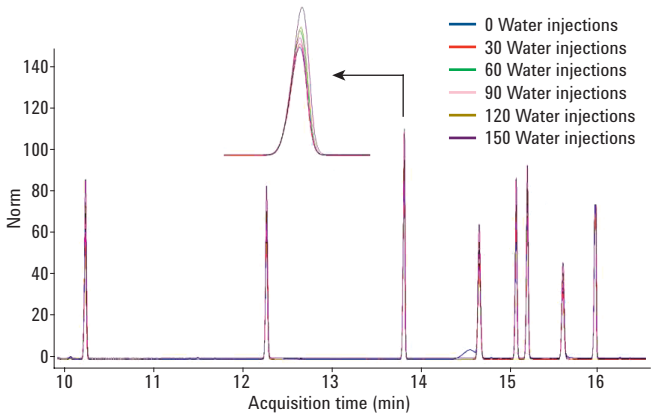

Figure 4. Repeated analysis of the Polar ISO mix on an Agilent J&W DB-WAX Ultra Inert GC column with 30 water injections (1 µL) between sample injections.

Applications

Chlorinated hydrocarbons in process water

Chlorinated hydrocarbons have many industrial applications, including the manufacture of industrial solvents and pesticides. Improper disposal practices or accidental spills of these compounds may pose a threat to environmental health. Thus, effective monitoring and control of these contaminants are essential. Figure 5 shows the analysis of chlorinated hydrocarbons in process water. Five chlorinated hydrocarbon compounds were detected, and all eluted with sharp and symmetrical peaks.

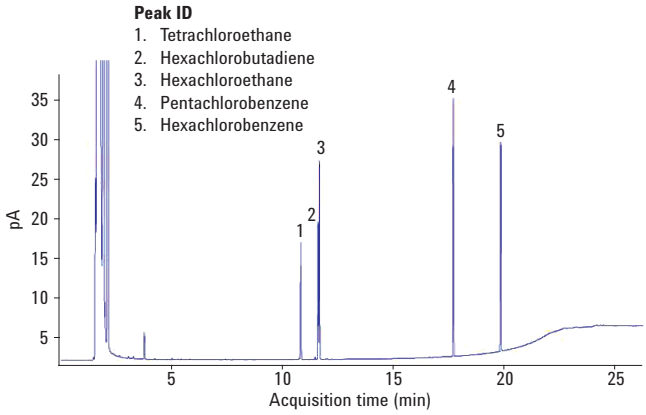

Figure 5. Separation of chlorinated hydrocarbon compounds in process water using an Agilent J&W DB-WAX Ultra Inert GC column.

Analysis of phenols in fuels and lubricants

A wide range of phenolic compounds including phenol and *tert*-butyl phenol have been found in the antioxidants package in fuels and lubricants. Figure 6 shows an overlay of three chromatograms of the separation of a phenol standard mix containing eight popular phenolic compounds in cyclohexane (100 ppm w/w each). Respectable separation and peak asymmetry were obtained for these compounds. The overlaid chromatograms from three replicate injections show excellent retention time repeatability for all components. These phenolic compounds are also commonly encountered in various industrial processes such as pulp and paper, dyes, and textiles.

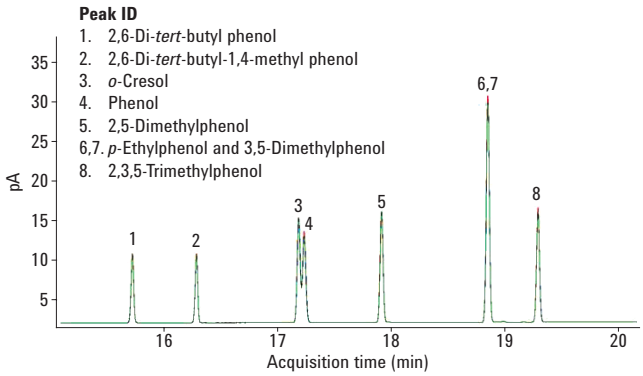

Figure 6. Analysis of phenols in fuels and lubricants using an Agilent J&W DB-WAX Ultra Inert GC column.

Nonradioactive bulk transfer compounds

Nonradioactive bulk transfer compounds can be added to products as unique product markers against counterfeiting and for product authentication. These compounds can be added into complex matrices, and are used for the assessment of sample integrity and source identification. Often, these compounds are functionalized, making the analysis challenging due to interactions between analytes and flowpath surfaces. Figure 7 shows the separation of butyl phenyl ether, dimethoxybenzene, and trimethoxybenzene. These are commonly used as marker compounds for petroleum hydrocarbons as well as for other fuels and oils. The DB-WAX Ultra Inert GC column delivered sharp and symmetrical peak shape for all three compounds. Retention times and peak shapes were consistent for three triplicate injections, as illustrated in the inset for butyl phenyl ether, indicating the stability and inertness of the DB-WAX Ultra Inert column.

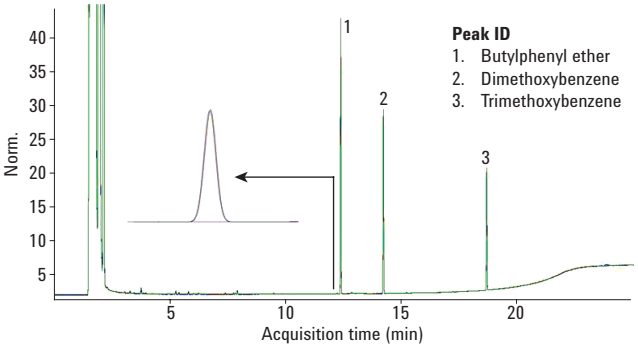

Figure 7. Analysis of fuel marker compounds using an Agilent J&W DB-WAX Ultra Inert GC column.

Select volatile organic compounds

Light hydrocarbons of industrial importance can be active and adsorptive, making the analysis of these molecules problematic, with tailing peaks and loss of response. Therefore, an inert column is critical for accurate quantification, especially for components at trace levels. Figure 8 demonstrates that the new stationary phase showed a high degree of inertness for volatile compounds, even with highly active compounds such as acetaldehyde (Peak 6). This inert column provides excellent peak shapes, even at low concentrations (0.5–1 ppm, blue trace), allowing for easier integration and more reliable quantification at low levels.

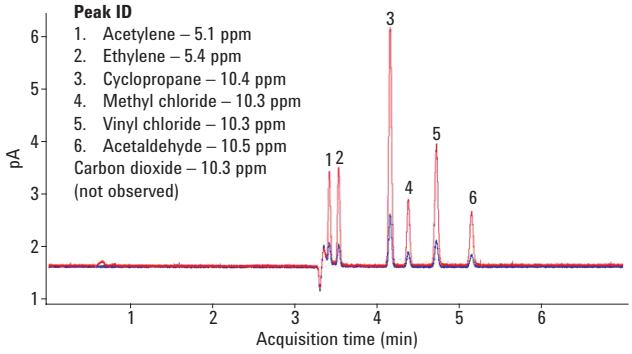

Figure 8. Analysis of volatile organic compounds using an Agilent J&W DB-WAX Ultra Inert GC column. Concentrations are for the red trace chromatogram. The blue trace is a 1 to 10 dilution of the gas standard (0.5–1 ppm range).

Constrains – highly basic compounds

The analysis of highly basic compounds, such as amines, is a challenging chromatographic application due to their reactivity and adsorption to active surfaces. As demonstrated in Figure 9, mono-ethanolamine (MEA) and methyl diethanolamine (MDEA) exhibited severe peak tailing due to interaction between analytes and the stationary phase.

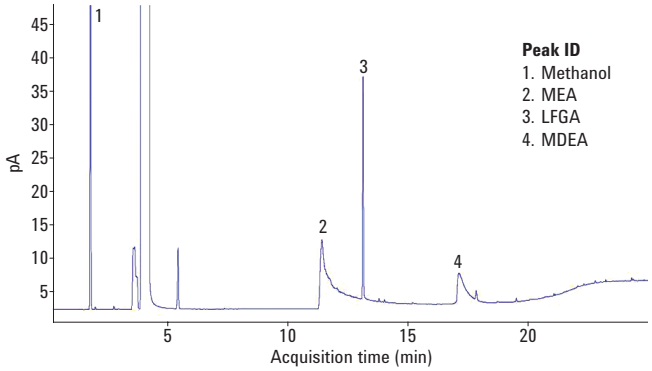

Figure 9. Analysis of highly basic compounds using an Agilent J&W DB-WAX Ultra Inert GC column. LFGA: low freezing grade amine, MEA: mono-ethanolamine, MDEA: methyl diethanolamine.

Conclusions

The Agilent DB-WAX Ultra Inert column delivers improved performance over classical PEG stationary phases, giving better peak shapes and improved sensitivity for active compounds. The improvement in inertness contributes to the overall total inert flowpath. Assessment of hydrolysis and swelling of the stationary phase in aqueous injections demonstrated no loss in inertness, allowing for direct aqueous sample analysis. The DB-WAX Ultra Inert column was found suitable for use in various industrially significant applications for analysis of polar compounds due to its high degree of inertness. These applications included the determination of phenol and alkylated phenols used as antioxidants in fuels and lubricants, nonradioactive bulk transfer compounds such as fuel marker compounds, and volatile organic compounds. The column phase can also be used for both multidimensional and comprehensive gas chromatography to enhance selectivity and chromatographic system peak capacity per unit time.

Acknowledgements

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