GC Analysis of Glycols in Toothpaste

Using Agilent J&W DB-Wax Ultra Inert Capillary GC Columns

Application Note

Flavors and Fragrances, Consumer Products

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Abstract

This application note demonstrates the excellent inertness performance of an Agilent J&W DB-Wax Ultra Inert GC column in the analysis of glycols in toothpaste. DB-Wax UI columns provide better column durability and more consistent analytical results compared with other PEG stationary phase GC columns.

Introduction

Typical toothpaste formulas are composed of various components including abrasives, fluoride, detergents, and a list of US-FDA approved flavors and sweeteners. Common moisturizers and sweeteners in toothpaste are propylene glycol, sorbitol, and glycerin.

Diethylene glycol (DEG) is an organic solvent often used in antifreeze [1,2], and unfortunately is chemically similar to propylene glycol and glycerin. DEG is classified as a toxic material, and has been indicated as a contributor in multiple systemic disorders leading to acute kidney failure and death [3]. DEG has physical and chemical properties close to the properties of glycerin and propylene glycol. Commercially, both glycerin and propylene glycol are more expensive than DEG. This facilitates the illegal use of DEG as a counterfeit substitute for glycerin in some nations, where it is sold as a component in cough syrup and toothpaste.

DEG is synthesized from the reaction of ethylene oxide with ethylene glycol, therefore, DEG can contain ethylene glycol (EG), a toxic impurity [4]. The US-FDA is concerned about potential risks from chronic exposure to DEG. There is also a concern, in certain populations, of DEG exposure to children and individuals with kidney or liver disease. DEG in toothpaste has a low but meaningful risk of toxicity and injury. The US-FDA has issued a recommended method to determine the levels of DEG and EG in toothpastes [5].

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Low levels of DEG, EG, 1,2-propanediol, 1, 3-propanediol, and glycerin were tested in this method. Due to the chemical properties of these compounds, particularly the multiple active hydroxyl (-OH) functional groups, their peaks often exhibit tailing when analyzed using traditional polyethylene glycol (PEG) stationary phase GC columns. Inertness of the column is important to achieve consistent and reliable results. Agilent J&W DB-Wax Ultra Inert columns are engineered for better peak shapes, and are rigorously tested with demanding probes to verify best-in-class inertness. This application note demonstrates the use of J&W DB-Wax Ultra Inert columns in the analysis of the active compounds in toothpaste with GC/MSD. It also compares the performance with PEG columns from other suppliers.

Experimental

The sample preparation was carried out according to the US FDA method [5]. The toothpaste sample was obtained from a local supermarket.

Chemicals and reagents

All reagents and solvents were HPLC or analytical grade. Acetonitrile (ACN) was from J&K Scientific (Beijing, China). Water was from J. T. Baker. Chemicals including 1,2-propanediol, 1,3-propanediol, ethylene glycol (EG), diethylene glycol (DEG), and glycerin were from ANPEL Scientific Instrument Co. Ltd (Shanghai, China).

Solutions and standards

Internal standard (IS)

A 1, 3-propanediol solution was prepared at 5.0 mg/mL in 50% (v/v) aqueous acetonitrile.

Mixed standard

DEG and EG were prepared in 50% (v/v) aqueous acetonitrile to give 5.0 mg/mL of each component.

Low standards

The mixed standard was diluted to 0.1 mg/mL of each analyte, and 0.50 mL of this standard was transferred to the autosampler vial, followed by the addition of 0.05 mL of internal standard.

High standards

The mixed standard was diluted to 0.5 mg/mL of each analyte, and 0.50 mL of this standard was transferred to the autosampler vial, followed by the addition of 0.05 mL of internal standard.

Performance test sample

Low standard, 0.1 mg/mL of each analyte including 1,2-propanediol, 1,3-propanediol (internal standard), DEG, EG, and glycerin was prepared in 50% (v/v) aqueous acetonitrile.

Sample preparation

Matrix blank

Approximately 1.0 g of toothpaste was weighed into a 15 mL polypropylene centrifuge tube.

Five milliliters of water was added, then vortexed for 1 minute. Foam started to appear, and 2 × 2.5 mL of acetonitrile was added to suppress the foam. The sample was mixed thoroughly, and centrifuged at 4,000 rpm for 10 minutes. Then, 0.50 mL of the supernatant was transferred to an autosampler vial, to which 0.05 mL of the internal standard was added.

Spiked sample

Approximately 1.0 g of toothpaste was weighed into a 15 mL polypropylene centrifuge tube. Then, 0.20 mL of mixed standard was added. The rest of the procedure was followed as previously described.

Instrumentation

Table 1 shows the instruments and conditions, and Table 2 lists the consumable supplies flow path.

Table 1. Conditions.

Parameter	Value
GC system	Agilent 7890B GC with an Agilent 5977A Series GC/MSD System
Column	Agilent J&W DB-Wax UI, 30 m × 0.25 mm, 0.25 µm (p/n 122–7032UI) Wax columns from other suppliers, 30 m × 0.25 mm, 0.25 µm
Tubing	Agilent Ultimate Plus deactivated FS tubing, 5 m × 0.25 mm (p/n CP802505)
Autosampler	Agilent 7683B autosampler and sample tray, 5 µL syringe (p/n G4513-80213), 1 µL injection volume
Carrier gas	Helium, 35 cm/s constant flow mode
Inlet	Split/splitless, 250 °C, split ratio 20:1
Oven	100 °C (1 min) to 250 °C at 10 °C/min (hold 4.00 min)
MSD	Agilent 5977A Series GC/MSD System
Solvent delay	4.0 min
MS temp	230 °C (source), 150 °C (quad)
Transfer Line	250 °C
MS	EI, Scan mode, Scan 29–400 amu

Table 2. Flow path supplies.

Parameter	Value
Vials	Amber, write-on spot, certified, 2 mL, screw top vial packs (p/n 5182–0554)
Septa	Nonstick BTO septa (p/n 5183–4757)
Column nut	Self-tightening, inlet/detector (p/n 5190–6194) Self-tightening, for MS interface (p/n 5190–5233)
Internal nut	CFT capillary fitting (p/n G2855-20530)
Union	Ultimate union (p/n G3182-60581)
Ferrules	15% graphite: 85% Vespel, short, 0.4 mm id, for 0.1 to 0.25 mm columns (10/pk, p/n 5181–3323) UltiMetal Plus Flexible Metal, for 0.1 to 0.25 mm columns (10/pk, p/n G3188-27501)
Liner	Agilent Ultra Inert split liner with glass wool (p/n 5190–2295)
Inlet seal	Ultra Inert, gold-plated, with washer (p/n 5190–6144)

Results and Discussion

The purpose of these tests was to evaluate the inertness performance of Agilent J&W DB-Wax Ultra Inert columns relative to Wax columns from other suppliers, using a typical toothpaste analysis.

Toothpaste analysis

Glycerin and propylene glycol (PG) are widely used in toothpaste. Glycerin, PG, DEG, and EG have similar physical properties, such as sweetness and viscosity, which facilitates the adulteration process. DEG and EG are target compounds for this analysis, because they are known poisons that are commonly used as industrial solvents and in antifreeze solutions. DEG and EG should not be found in toothpaste formulations. 1,2-propanediol is a related compound, and glycerin is a common component found in toothpaste. 1,3-propanediol is used as an internal standard (IS) according to the US-FDA method. Due to the multiple active hydroxyl (-OH) functional groups in these compounds, traditionally it has been quite challenging to achieve good peak shape. Figure 1 shows the symmetrical peak shapes for these active compounds at 0.1 mg/mL. This symmetry indicates the high level of inertness of the J&W DB-Wax Ultra Inert GC column.

The US-FDA method uses a 30 m × 0.25 mm, 0.25 µm Wax column with a 5 m guard column to evaluate the presence of DEG and EG at 1 mg/g (0.1 % by weight) and above. A 5 m × 0.25 mm Agilent Ultimate Plus deactivated FS tubing was used as a guard column connected with an Agilent DB-Wax Ultra Inert 30 m × 0.25 mm, 0.25 µm GC column in this application. Low (0.1 mg/mL) and high standards (0.5 mg/mL) were analyzed using GC/MSD in full scan mode with an Agilent J&W DB-Wax UI GC column and a DB-Wax UI GC column attached to a 5 m guard column. The DB-Wax UI GC column with guard column delivered similar symmetrical peak shape and response of EG and DEG as a single DB-Wax UI GC column when analyzing low and high standards. This is a result of the advanced Agilent inert flow path technology. 1,3-propanediol is a challenging compound, but the peak exhibited relatively little tailing on a DB-Wax UI GC column with the guard column in-line.

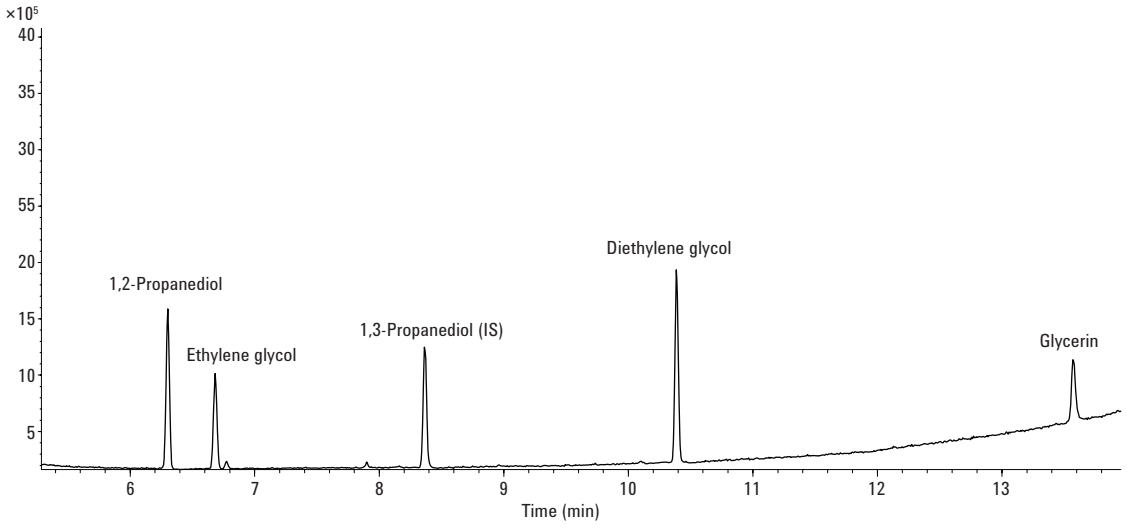

Figure 1. GC/MS total ion chromatogram of analytes and related compounds at a concentration of 0.1 mg/mL. Performed on an Agilent J&W DB-Wax Ultra Inert, 30 m × 0.25 mm, 0.25 µm GC column.

Figure 2 compares the results observed with and without the guard column installed on a DB-Wax Ultra Inert 30 m × 0.25 mm, 0.25 µm GC column.

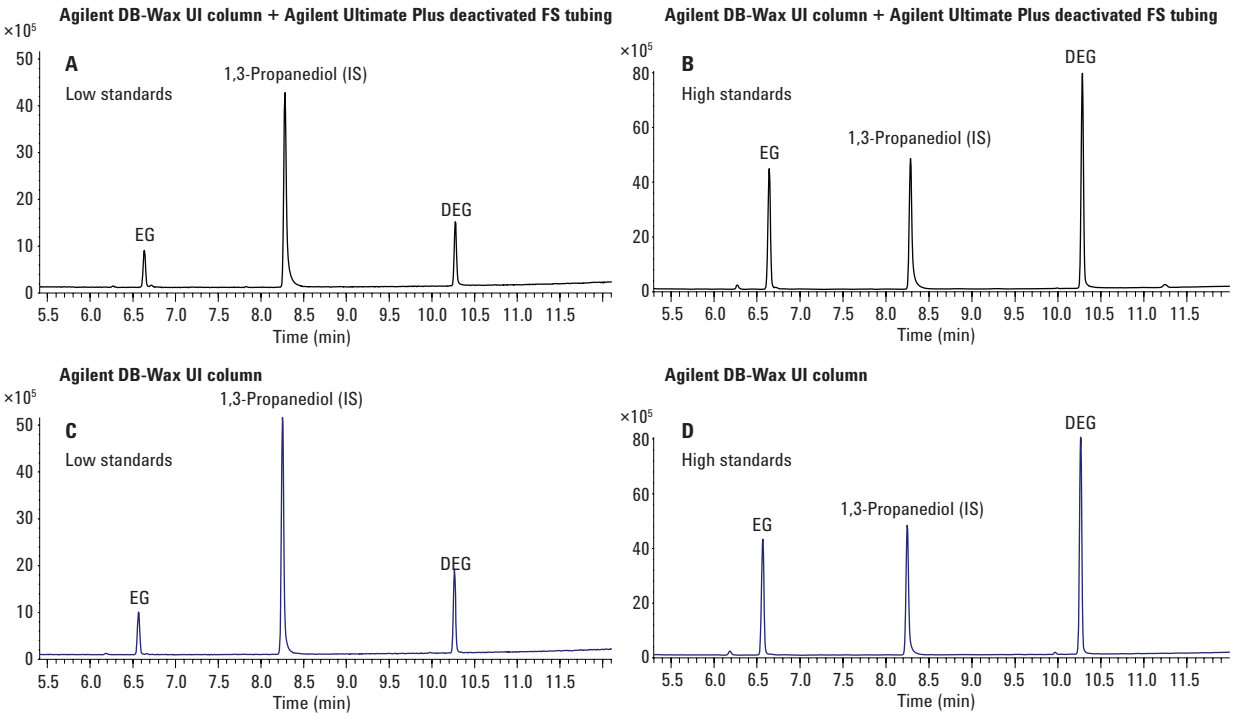

Figure 2. GC/MS total ion chromatograms of low (0.1 mg/mL) and high standards (0.5 mg/mL), on an Agilent DB-Wax Ultra Inert GC column attached to a guard column, and an Agilent DB-WAX Ultra Inert GC column not attached to a guard column.

A 1 mg/g amount of DEG and EG spiked into a toothpaste sample were analyzed using a DB-Wax UI GC column with a guard column. Figure 3 shows the chromatograms of matrix blank and spiked sample. No DEG and EG was present in the toothpaste matrix blank sample. Although many components including menthyl acetate, 1,2-propanediol, menthol, glycerin, thymol, and methylparaben were identified in the samples, they did not interfere with analysis of DEG and EG. Excellent peak shape was observed for all these active compounds in Figure 3.

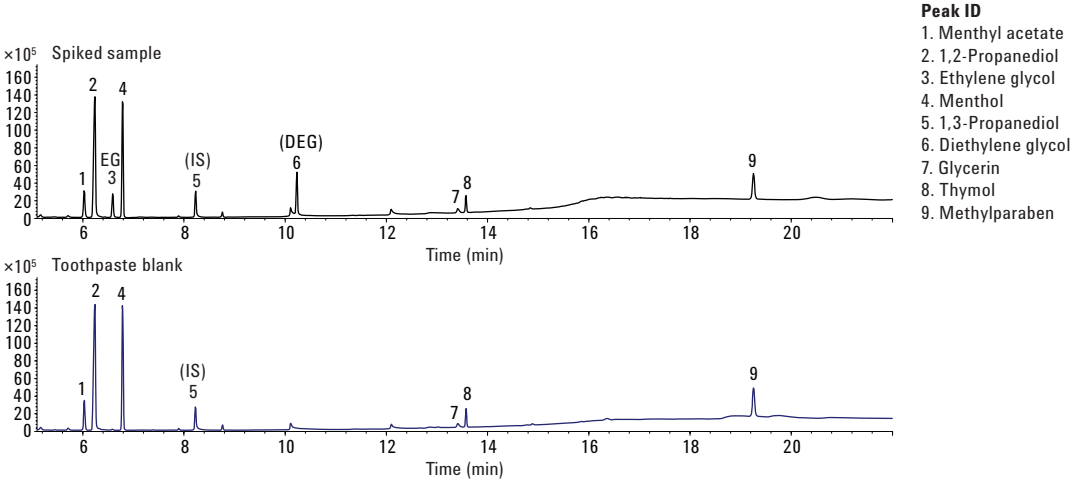

Figure 3. GC/MS total ion chromatogram of spike 1.0 mg/g of EG and DEG in toothpaste sample and toothpaste matrix blank

Comparison with other Wax columns

All columns were tested using a performance test sample. This consisted of 0.1 mg/mL of each analyte including 1,2-propanediol, 1,3-propanediol, DEG, EG, and glycerin prepared in 50% (v/v) aqueous acetonitrile. The system was inspected, and carefully cleaned, if necessary, before each test. For consistency, new gold seals and liners were used for each test.

Normally, the first analysis on each Wax column showed an acceptable or good peak shape. After a few injections, the peak shapes of EG, DEG, and 1,2-propanediol changed little. However, the peak shapes of 1,3-propanediol (peak 3) and glycerin (peak 5) deteriorated to different degrees due to the variable inertness performance and thermal stability of each Wax column.

According to the US-FDA method, the final oven temperature of this application is 250 °C. Inertness performance of Wax columns from different suppliers deteriorated differently after conditioning the column for more than 2 hours to get an acceptable baseline.

Figures 4 and 5 show comparison results. In the first few injections, wax columns from Supplier A and Supplier B initially showed essentially similar performance as DB-Wax UI. After 10 injections, there was noticeable tailing and reduced response of 1,3-propanediol in the chromatograms for suppliers A and B.

High inertness and the improved thermal longevity of the DB-Wax UI provided better peak shape and more durable analytical results than was achievable on the other Wax columns evaluated.

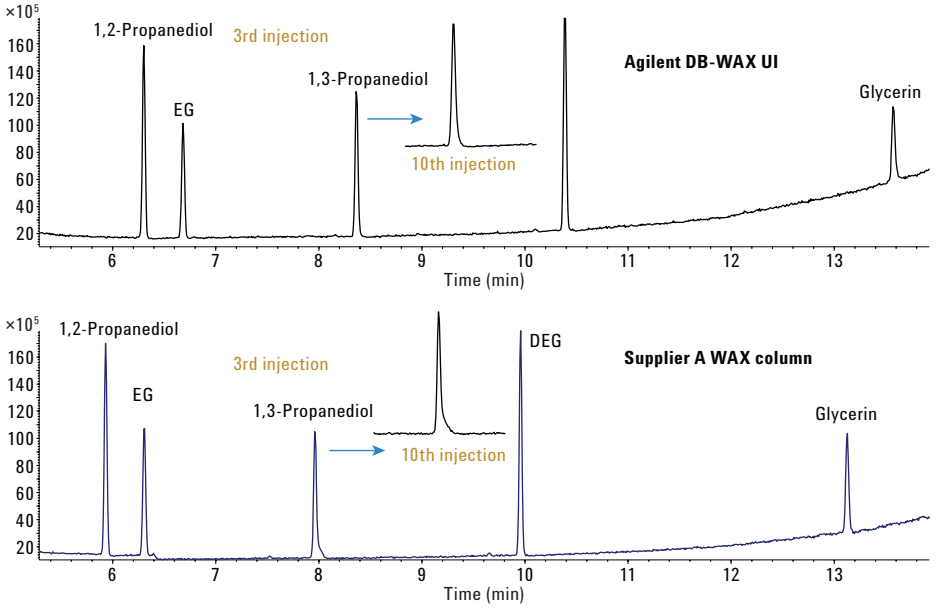

Figure 4. Chromatograms of performance test mixture on an Agilent DB-WAX UI and a Wax column from Supplier "A".

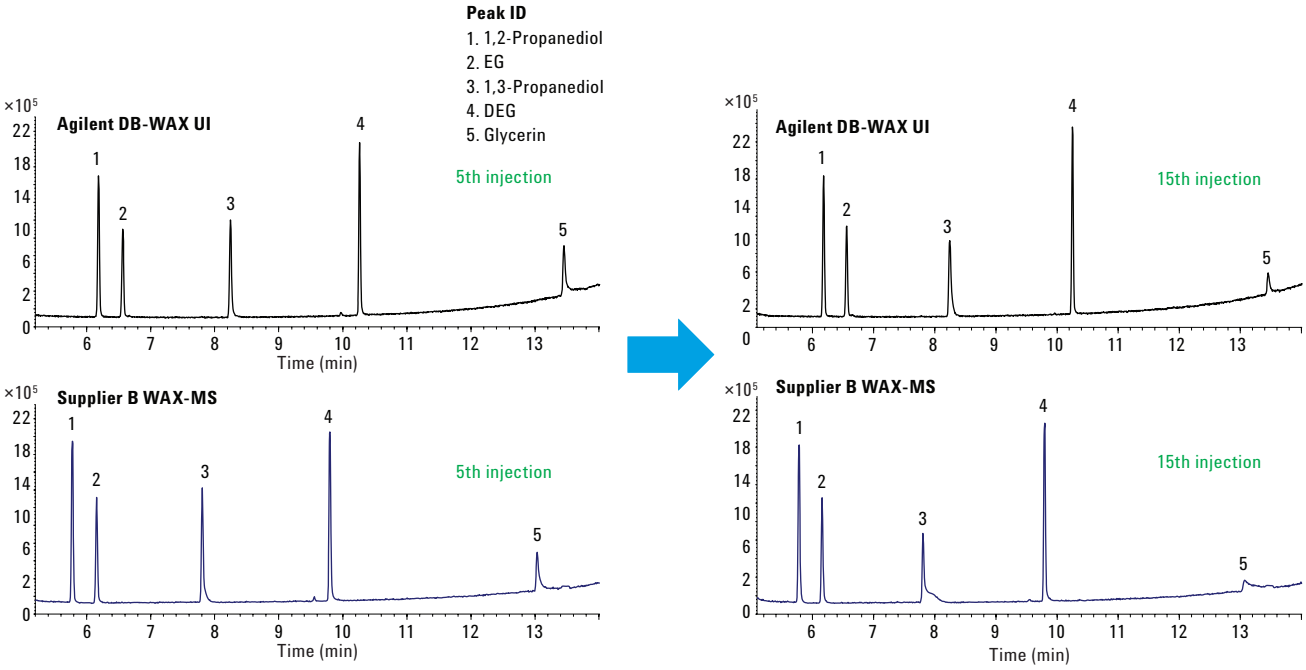

Figure 5. Chromatograms of performance test mixture on an Agilent DB-WAX UI and a Wax column from Supplier B.

Conclusions

Inertness performance of Agilent J&W DB-Wax Ultra inert GC column was evaluated by analyzing glycols in toothpaste samples using GC/MSD.

Compared with other vendors' Wax columns, J&W DB-Wax Ultra inert GC columns delivered better peak shape, and more durable and consistent analytical results. Combining all the inert flow path components, including Agilent Ultimate Plus Deactivated FS tubing as a guard column, it ensures excellent performance and reliable results for active compound analysis.

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