

GC-MS Analysis of Diethylene Glycol and Ethylene Glycol in Toothpaste Using Thermo Scientific TraceGOLD GC Column with SafeGuard

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Abstract

This application note demonstrates the semi-quantitative analysis of diethylene glycol (DEG) and ethylene glycol (EG) according to the FDA method at levels of 0.5 mg/g in toothpaste.

Two approaches have been used to determine DEG and EG in toothpaste at a low level of 0.1 mg/mL in a full scan mode.

1. Thermo Scientific TraceGOLD TG-WaxMS GC column with 5m SafeGuard, a continuous 30m phased analytical column with an integrated guard column which is un-phased.

2. Thermo Scientific TraceGOLD™ Guard column attached to the analytical column via a press-fit.

The FDA method is evaluated using both column formats and compared for the suitability of semi-quantitation of DEG and EG in toothpaste.

Introduction

In the past health officials have warned consumers not to use certain brands of toothpastes that have been shown to be adulterated by unsafe additives. One such additive is the sweet tasting but poisonous diethylene glycol (DEG). This is a common component of automotive anti-freeze and its ingestion has caused many deaths globally. Although the use of DEG in toothpaste has been banned there are unlicensed chemical factories in parts of the world that continue to adulterate their healthcare products with DEG. The FDA has issued a recommended method to determine the levels of DEG and ethylene glycol (EG) in toothpastes. The component EG has low toxicity, and is a common component found in toothpaste which is frequently combined with Glycerin.

The work presented in this application note uses GC-MS to analyse DEG and EG in toothpaste. The work is based on the FDA method¹ which uses a 30 m x 0.25 mm x 0.25 µm wax column with a 5 m guard and this method evaluates the presence of DEG and EG at 1 mg/g (0.1% by weight) and above.

The performance of the method was compared on a TraceGOLD TG-WaxMS GC column with 5m SafeGuard and a TG-WaxMS GC column attached to a 5m Guard column via a press-fit.



Experimental Details

Preparation of Samples

The sample preparation was carried out according to the FDA method¹. Branded toothpaste was obtained from a local pharmacy.

- **Uncontaminated Sample:**
1 g of toothpaste was weighed into a 15 mL propylene centrifuge tube and 5 mL of water was added and mixed well. Foam starts to appear and to this 2 x 2.5 mL of acetonitrile was then added to suppress the foam. The sample was mixed thoroughly and centrifuged and 500 µL of the extract was placed in the autosampler vial followed by the addition of 50 µL of internal standard.
- **Internal Standard (IS):**
1, 3-propane diol prepared at 5.0 mg/mL in 1:1 acetonitrile/water.
- **Mixed Standard:**
Equal volumes of 10 mg/mL DEG and EG was prepared in 1:1 acetonitrile/water to give 5.0 mg/mL of each standard.
- **Spiked Sample:**
1 g of un-contaminated toothpaste was weighed into a 15 mL propylene centrifuge tube and 200 µL of mixed standard was added. The rest of the procedure was followed described above.
- **Low Standards:**
The mixed standard was diluted to 0.1 mg/mL and 500 µL was transferred to the autosampler vial followed by the addition of 50 µL of internal standard.
- **High Standards:**
The mixed standard was diluted to 0.5 mg/mL and 500 µL was transferred to the autosampler vial followed by the addition of 50 µL of internal standard.
- **QC Check:**
Low standard - 0.1 mg of each analyte including 1,2-Propane diol (a related compound), 1,3-propane diol (internal standard), DEG, EG, and glycerin (common component found in toothpaste) was prepared in 1:1 acetonitrile/water to show the necessary sensitivity of the instrument.

High standard – 0.5 mg/mL of each component was prepared to provide a basis for semi-quantitative evaluation of the sample.

Key Words

- TraceGOLD™ TG-WaxMS GC Column
- TraceGOLD TG-WaxMS with 5m SafeGuard
- TraceGOLD Guard
- Press-fit
- Toothpaste
- Diethylene Glycol (DEG)
- Ethylene Glycol (EG)

Separation Conditions**Part Number**

Instrumentation:	Thermo Scientific TRACE GC Ultra	
Columns:	TraceGOLD TG-WaxMS with 5m SafeGuard, 30 m x 0.25 mm x 0.25 µm	26088-1425
	TraceGOLD TG-WaxMS, 30 m x 0.25 mm x 0.25 µm	26088-1420
	TraceGOLD capillary guard column 5m x 0.25 mm Guard Column	26050-0525
	Press-Fit	64000-001
Septum:	BTO, 17 mm	31303211
Liner:	Focus Splitless liner, 5 x 8 mm	45350033
Column ferrules:	100% Graphite ferrules for TRACE injector/detector	29053488
Injection syringe:	10 µL Fixed needle syringe for a TriPlus Autosampler	36500525
Vials and caps:	PTFE lined 2 mL Screw Vial kit	60180-599
Carrier gas:	Helium	
Split flow:	20 mL/minute	
Column flow:	1.0 mL/minute, Constant flow	
Split ratio:	20:1	
Oven temperature:	100 °C (1 minute), 10 °C/minute, 250 °C (4 minute)	
Injector type:	Split/Splitless	
Injector mode:	Split	
Injector temperature:	250 °C	
Thermo Scientific ISQ Mass Spectrometer		
Transferline Temperature:	250 °C	
Source Temperature:	230 °C	
Ionisation Mode:	EI	
Scan Parameters:	29-400 amu	
Scan time:	0.25 seconds	
Solvent Delay:	4 minutes	
Thermo Scientific TriPlus Autosampler		
Injection Volume:	1 µL	
Pre and Post Injection		
Dwell Time:	5 seconds	

Results

The FDA method was evaluated using the TraceGOLD TG-WaxMS attached to a TraceGOLD 5m Guard column via press-fit and a TraceGOLD TG-WaxMS GC Column with SafeGuard. The DEG and EG spiked into toothpaste was quantified and the analyses was carried out in a full scan mode. The TIC of analytes and related compounds found in toothpaste is shown in Figures 1 and 2, the identification of peaks in Table 1.

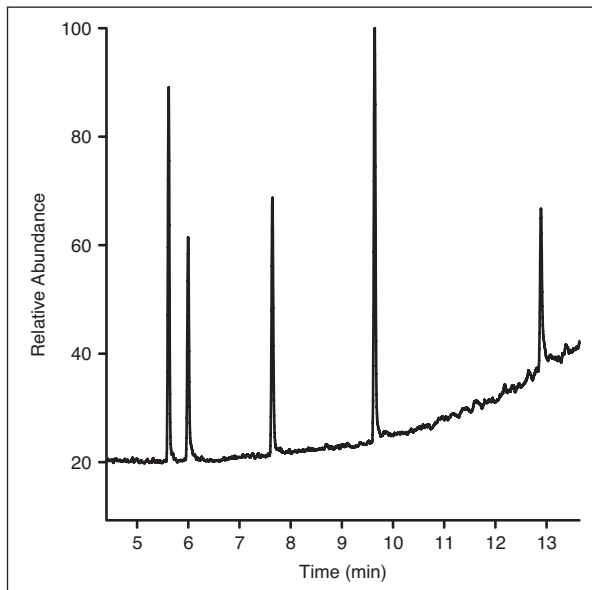


Figure 1: TIC of analytes at a concentration of 0.1 mg/mL on a TraceGOLD TG-WaxMS Safeguard

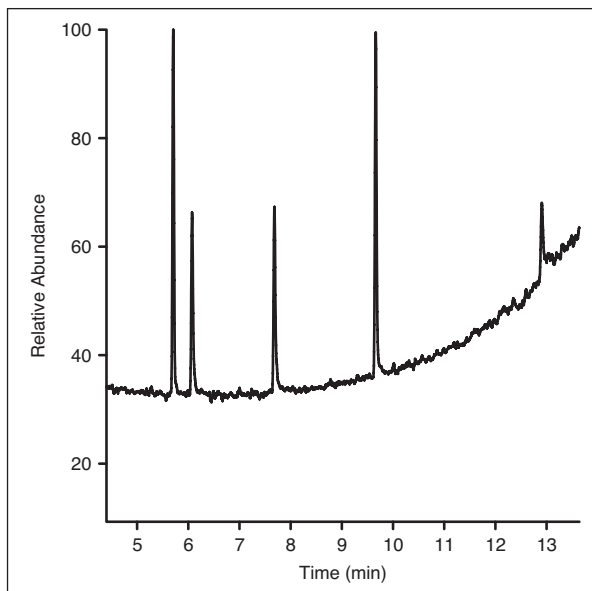


Figure 2: TIC of analytes at a concentration of 0.1 mg/mL on a TraceGOLD TG-WaxMS attached to a Guard column via a press-fit

Peak Number	Compound	Tr (min) (Figure 1)	Tr (min) (Figure 2)
1	1,2-Propane diol	5.99	5.71
2	Ethylene Glycol	6.37	6.07
3	1,3-propane diol (IS)	7.99	7.68
4	Diethylene glycol	10.00	9.66
5	Glycerin	13.15	12.90

Table 1: Retention times for each analytes at a concentration of 0.1mg/mL

Semi-quantification was achieved by calculating the integrated response using extracted ion chromatogram m/z 62 for ethylene glycol, m/z 75 for diethylene glycol and m/z 58 for 1,3-propane diol. The FDA method applies a formula to obtain the estimate for a semi-quantitative analysis for target analytes. In this case, Xcalibur software was used to calculate the spiked samples against the high standard solution and the estimate of the spiked target samples was obtained (see Table 2 for results). No DEG and EG was present in the un-spiked toothpaste.

Compound	Quan Ion	Concentration in Sample (% by weight*) Figure 1	Concentration in Sample (% by weight*) Figure 2
Ethylene Glycol	62	0.50	0.50
1,3-propane diol (IS)	58	-	-
Diethylene glycol	75	0.51	0.48

*The % weight estimate is calculated according to the FDA method using the spiked 0.5mg/mL standard solution in toothpaste.

Table 2: Estimated concentration of DEG and EG spiked at 0.5 mg/mL in toothpaste

In this comparison of both columns, the TraceGOLD GC column with SafeGuard column gave better signal/noise(s/n) ratio of glycerin of 47rms than TG-WaxMS attached to a Guard column via a press-fit which gave a lower s/n of 25 rms. The Safeguard column reduces any potential source of leaks and dead volume from the column connection and this improves the s/n ratio.

The analysis carried out in both column formats demonstrates that the FDA method is suitable to use with TraceGOLD TG-WaxMS columns for the semi-quantitative estimate for DEG and EG in toothpaste.

Conclusions

The TraceGOLD TG-WaxMS with SafeGuard gave better signal/noise of glycerol when compared on TG-WaxMS column attached to a Guard column via a press-fit for the analysis of DEG and EG at 0.5mg/g levels in toothpaste.

TraceGOLD TG-WaxMS can be used for the analysis of DEG, EG and related components according to the FDA method on both column formats.

References

[1] FDA method, Gas Chromatography-GC-MS Screening Procedure for the Presence of Diethylene Glycol and Ethylene Glycol in Toothpaste.

<http://www.fda.gov/Food/ScienceResearch/>

LaboratoryMethods/DrugChemicalResiduesMethodology/cum113209.htm

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