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Comparison of WCOT and PLOT Columns for the GC/MS Analysis of Benzene in Soft Drinks

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Key Words

- Trace PLOT TG-Bond Q
- TRACE TR-V1
- Benzene
- Soft Drinks

Overview

The FDA method for the quantitation of benzene in soft drinks allows for the use of two approaches:

1. A capillary 6% cyanopropylphenyl polysiloxane (polar) wall coated open tubular (WCOT) column with cryogenic trapping
2. A Porous Layer Open Tubular (PLOT) column fitted with headspace sampling.

We have evaluated the Thermo Scientific equivalent columns specified in the FDA method and compared these for their suitability in the quantification of benzene at low concentrations.

Introduction

The presence of benzene in soft drinks is a result of the reaction between sodium benzoate and ascorbic acid (vitamin C) under certain conditions of heat and light. Sodium benzoate is added as a preservative to prevent mold growing in the drinks and vitamin C may be used as an antioxidant or may be naturally present.

Benzene is widely known as a human carcinogen, therefore many regulatory bodies such as FDA, WHO, EPA and EU have established limits for benzene levels in food and drinking water. It is therefore necessary to have robust, reproducible and simple methods for the determination of benzene in soft drinks.

The work presented in this application note uses GC/MS with headspace sampling to analyse benzene in soft drinks. The work is based on the FDA method for determination of benzene in soft drinks and other beverages.[1] The FDA method uses cryogenic focussing at -50 °C prior to headspace GC/MS analysis. However, cryogenic focussing was not applied in this case but direct headspace analysis was performed.

The performance of the method on a 6% cyanopropyl-phenyl polysiloxane WCOT column is compared with that of a PLOT column. Traditional PLOT columns suffer from poor particle stability and very often these are released from the column causing blockages and flow irreproducibility. Thermo Scientific TracePLOT columns use a proprietary particle adsorption process which minimizes particle release and therefore improves chromatography. However, to ensure no particles entered the detector a particle trap was used between the analytical column and the MS detector.

Benzene in a carbonated energy drink is quantified by isotope dilution using benzene-d_6. A six-point calibration curve shows good method linearity on both types of columns. In this study it was also confirmed that benzene was not formed during analysis.

Methods

Sample Preparation

A non-branded carbonated energy drink which contained ascorbic acid and sodium benzoate, was obtained from a local supermarket. Calibration standards were prepared by weighing 10 g of water into a headspace vial and adding benzene to obtain concentrations of 0.5, 1.0, 2.5, 5.0, 10.0 and 20 ng/g. To each calibration standard 10 ng/g of internal standard benzene-d_6 was added. To determine the benzene in the carbonated soft drink, 10 g of the sample was weighed into the headspace vial to which 10 ng/g of internal standard was added.

Columns	Part Number
TRACE TR-V1, 30 m x 0.25 mm x 1.4 µm	260V332P
TracePLOT™ TG-Bond Q, 30 m x 0.32 mm x 10 µm	26004-6030
TracePLOT TG-Bond Q, 15 m x 0.32 mm x 10 µm	26004-6000
Particle Trap, 2.5 m x 0.32 mm	60180-860

The analytical column and the particle trap were connected via a glass fitting. This process takes place under high temperature and pressure.

GC-MS Conditions

Thermo Scientific TriPlus Headspace Autosampler	
Sample Volume	1 mL
Sample Analysis Time	30 min
Agitator Temperature	60 °C
Incubation Time	15 min
Agitator Shake	On 15 s, Off 15 s
Syringe Temperature	100 °C
Post Injection Flush	30 s

Thermo Scientific TRACE GC Ultra

Oven Program	40 °C, 7.5 °C/min, 210 °C (7.33 min)
Equilibration Time	0.5 min
Injector	200 °C, Split
Split Ratio	10
Column Flow	1.0 mL/min, constant flow for TRACE TR-V1 column 1.7 mL/min, constant flow for TracePLOT TG-Bond Q15 m column 1.2 mL/min, constant flow for TracePLOT TG-Bond Q 30 m column
Transfer Line Temperature	230 °C

Thermo Scientific DSQ II MS

Source Temperature	200 °C
Ion Volume	Closed EI
Emission Current	50 µA
Electron Energy	-70 V
Filament Delay	5.5 min
Scan Parameters	Selected Ion monitoring: *m/z* 51, 77 and 78 for benzene and *m/z* 52, 82, and 84 for benzene-d_6
Dwell Time	100 ms

Consumables	Part Number
Thermo Scientific BTO 17 mm septa	31303211
5 mm ID Focus Liner, 105 mm long	453T1905
Liner graphite seal	29033406
2.5 mL headspace syringe	36503006
Graphite ferrules to fit 0.32 mm ID columns	29053488
Graphite ferrules to fit 25 mm ID columns	29053487
Graphite/vespel 0.32 mm ID ferrules for GC/MS interface	29033496
Graphite/vespel 25 mm ID ferrules for GC/MS interface	29033497
20 mL clear crimp top vial	60180-506
Aluminum 20 mm cap and Si/PTFE seal	60180-511

Results and Discussion

We compared the analysis of benzene in a carbonated soft drink using the two columns provided as alternatives in the FDA method.

Capillary WCOT Column

The FDA method allows for use of a polar capillary WCOT column with cryogenic focusing at -50 °C. We evaluated a method in which the Thermo Scientific TRACE GC Ultra and DSQ II fitted with headspace auto-sampler and a TRACE TR-V1 GC column demonstrated a detection limit of 1.54 ng/g (in matrix), good peak shape (Figure 1a) and good detector linearity without the need for cryogenic trapping.

PLOT Column

The FDA also allows for use of PLOT column, thereby providing a legitimate alternative when cryogenic focusing is unavailable in a laboratory. When we tested this approach using a TracePLOT TG-BOND Q column, we observed a detection limit of 2.45 ng/g (in matrix) and good detector linearity (Figure 1b and 2a, Table 1). We also tested a column that was double the length stated in the FDA method (30 m). The larger pressure drop across the column resulted in a lower pressure in the MS, which we attributed to an observed increase in the sensitivity (Figure 1c and Table 1).

	Linearity R^2		Limits of Detection		Limits of Determination	
Column	Water	Drink	Water ng/g	Drink ng/g	Water ng/g	Drink ng/g
TR-V1	1.000	0.998	0.16	1.54	0.52	5.15
TG-BOND Q 15 m	0.999	0.994	0.81	2.45	2.69	8.18
TG-BOND Q 30 m	0.999	0.997	0.78	1.77	2.60	5.91

Table 1: Comparison of the calibration results of 3 methods used to quantify benzene in soft drinks

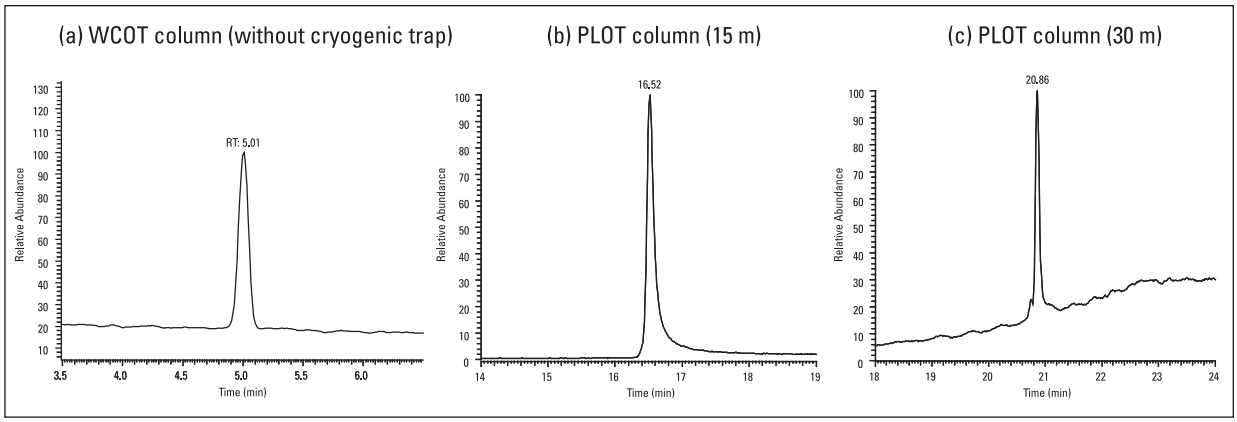

Figure 1: SIM of lower standard 0.5 ng/g of benzene in water

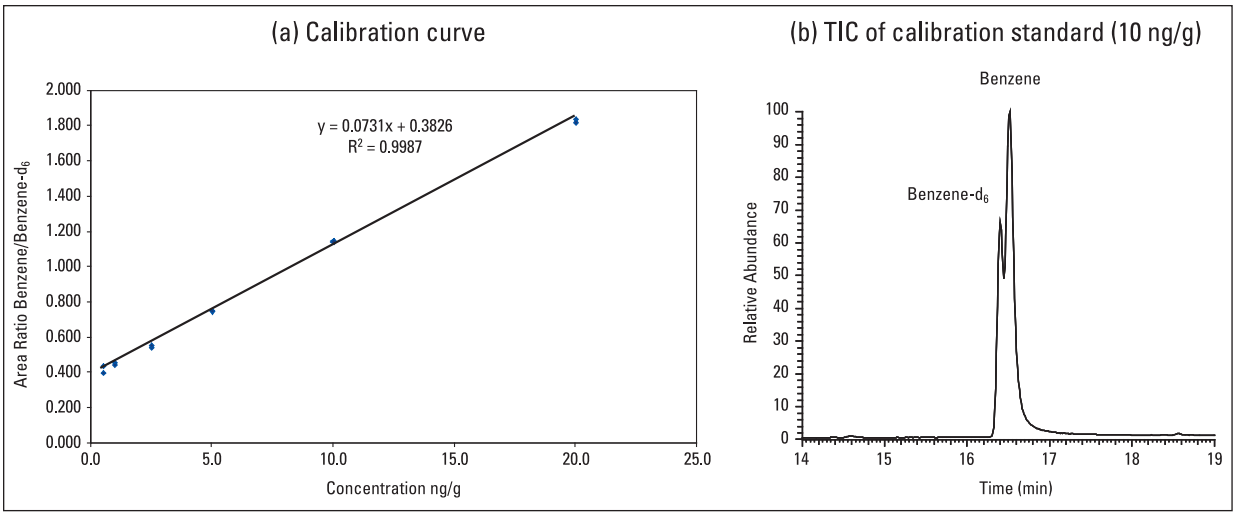

Figure 2: Calibration curve of benzene in water and TIC of 10 ng/g standard using TracePLOT TG-BOND Q column (15 m)

Conclusions

- It is possible to obtain good retention and sensitivity when quantifying benzene in soft drinks using the FDA polar WCOT GC column, without the cryogenic focusing stipulated in the method.
- The PLOT GC columns provides good sensitivity when using the FDA method.
- Better sensitivity can be achieved with lower MS pressures, which are best achieved with a longer PLOT column than that stated in the FDA method.

References

1. FDA Method, Determination of Benzene in Soft Drinks and Other Beverages. *http://www.fda.gov/Food/FoodSafety/FoodContaminantsAdulteration/ChemicalContaminants/Benzene/ucm055179.htm*

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