Achieving Low-Level Detection of Benzene in Beverages with an Automated Headspace Vial Sampler

Application Note

Abstract

Eight commercially available beverage samples were selected for low-level detection of benzene by static headspace analysis. This study will use the Teledyne Tekmar HT3 Automated Headspace Vial Sampler to analyze parts per trillion (ppt) levels of benzene in beverages. A GC/MS system will be employed in full scan/SIM mode for separation and detection of benzene, as well as other volatile compounds.

The HT3 was capable of detecting 0.05 parts per billion (ppb) of benzene in the samples with excellent linearity from 0.05 to 20 ppb. The 0.05 ppb quantitation level achieved is 20 times lower than the European benzene drinking water requirement of 1 ppb.

Introduction

Beverages containing sodium or potassium benzoate in combination with ascorbic acid have the potential to form benzene. Headspace detection methods have been developed by numerous agencies, including the International Council of Beverages Associations[1] and the US FDA[2].

Experimental-Instrument Conditions

A recent Tekmar application note[3] indicated that using the HT3 with a modern mass spectrometer would yield parts per trillion detection levels of environmentally regulated compounds, including benzene, as low as 0.020 ppb in drinking water. The HT3 was paired with a GC/MS system equipped with turbo molecular pump, a Restek Rtx®-502.2 column, and Helium as the carrier gas. Parameters for these systems are listed in Table I and Table II.

Table I: HT3 Automated Headspace Vial Sampler Conditions

Parameters	Variable	Parameters	Variable
Constant Heat Time	On	Mixing Time	10.00 min
GC Cycle Time	32.00 min	Mixing Level	Level 10
Valve Oven Temp	120 °C	Mixer Stabilize Time	3.00 min
Transfer Line Temp	120 °C	Pressurize	12.0 psig
Standby Flow Rate	100 mL/min	Pressurize Time	1.00 min
Platen/Sample Temp	70 °C	Pressurize Equil. Time	0.25 min
Platen Temp Equil. Time	0.50 min	Loop Fill Pressure	9.0 psig
Sample Equil. Time	10.00 min	Loop Fill Time	0.30 min
Mixer	On	Inject Time	1.00 min

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Table II: GC/MS Parameters	
GC/MS Parameters	
Column	Rtx®-502.2, 30 m, 0.25 mm ID, 1.4 µm dF
Oven Program	60 °C for 2 min, 8 °C/min to 150 °C then 20 °C/min to 260 °C for 5 min, run time 23.75 min
Inlet:	Temperature 200 °C, Split Ratio 30:1, Constant Flow 1.0 m L/min
Transfer Line	Temperature 220 °C
Mass Spec	Start Time 1.75 minutes, Full Scan,1.75 min to 23.75 min, and Selected Ion Monitoring (SIM), 4.0 to 6.0 min, 51.0 m/z, 52.0 m/z, 56.0 m/z, 77.0 m/z, 78.0 m/z, and 84.0 m/z, Source Temperature 230 °C

Standard Preparation

A benzene stock standard of 0.5 ppm in water and an internal standard of 4.2 ppb benzene-d6 in methanol were prepared following the FDA method. A standard curve from 0.050 ppb to 20 ppb was prepared by pipeting the 0.5 ppm standard into 10 g of reagent water in a 22 mL headspace vial containing internal standard. 10 µL of the benzene-d6 standard was added to all vials, instead of 25 µL per the FDA method.

Commercially available beverage samples with the potential to contain benzoate salts were selected. The selection included: four carbonated beverages, two energy/vitamin drinks and two nonalcoholic cocktail mixes. 10 g of each sample was weighed into a 22 mL headspace vial and 10 µL internal standard solution was added to each.

The use of sodium chloride, as well as a sodium hydroxide solution for carbonated beverages (suggested by the International Council of Beverages Association) was not tested in this application note.

Calibration Curves and Data

The standards and blanks were analyzed with the HT3 and GC/MS parameters listed in Table I and II. Figure 1 compares the SIM chromatogram of the benzene 78 m/z quantitation mass of blank water and the 0.050 ppb standard, both with benzene-d6 internal standard. A lower concentration of benzene-d6 internal standard was used to minimize this mass 78 m/z interference of benzene. Figure 2 is a head to tail comparison of the reference spectra for benzene to benzene-d6 from the NIST 2.0 library[4].

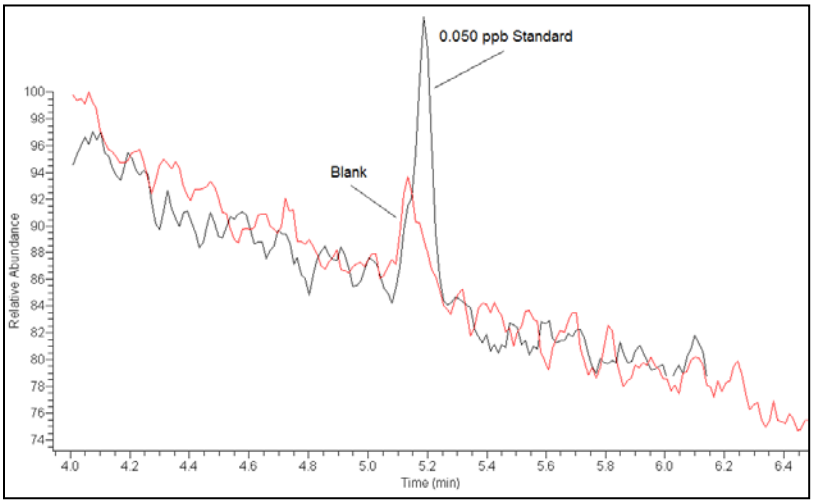

Figure 1: Comparison of the SIM Chromatogram Mass 78 m/z for Blank Water and the 0.050 ppb Standard, Both with Internal Standard.

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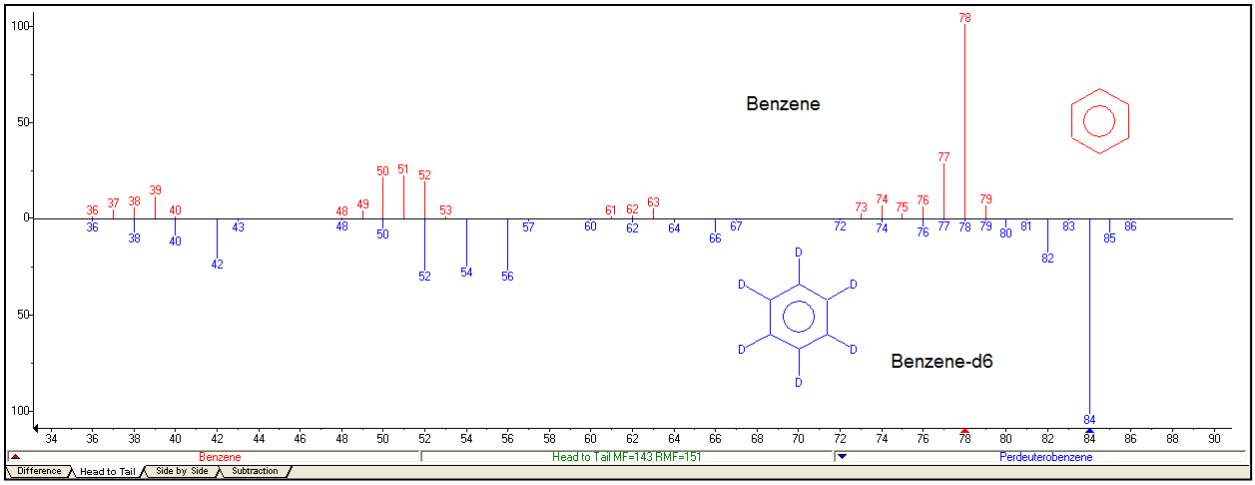

Figure 2: Head to Tail Comparison of Benzene to Benzene-d6.

Table III lists the response factor and linear calibration curve data for the 0.050 to 20 ppb benzene standards.

Table III: Mass Ion, Scan Rate, and Calculated Data for Benzene

Compound	Quant Mass	Dwell Time	Rf %RSD 0.050 ppb to 20 ppb	Linearity r^2
Benzene	78	50	8.7	0.9987

Beverage Preparation and Data

10 g of each beverage sample was transferred to 22 mL headspace vials and 10 µL of the benzene-d6 internal standard solution was added to each. The vials were sealed with crimp top caps with silicon septa, and the benzene concentration calculated. The results of the analysis are shown in Table IV.

Table IV: Calculated Benzene Concentration for the Sampled Beverages and Potential Benzene Forming Compounds (Determined by Label Content)

Beverage	Potential Benzene Compound	Benzene (ppb)
Soda A	None	ND
Diet Soda A	Potassium Benzoate	0.200
Soda B	None	ND
Soda C	Sodium Benzoate	0.177
Vitamin Enhanced Energy Drink	Sodium Benzoate	0.321
Energy Drink	Benzoic Acid	0.065
Sweet and Sour Mix	Sodium Benzoate	0.321
Margarita Mix	Sodium Benzoate	0.782

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Additional Qualitative/Quantitative Information

Because the static headspace analysis was conducted with a GC/MS in SIM/scan mode, additional qualitative and quantitative information useful to a QC laboratory was obtained. Figures 3 and 4 show a comparison of the total ion chromatograms with observed additional peaks.

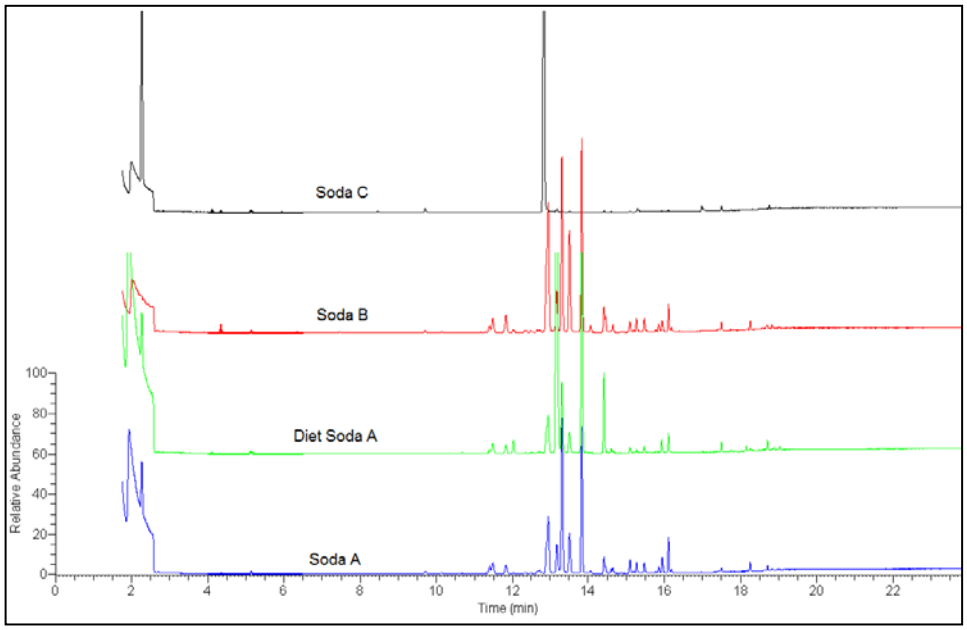

Figure 3: Overlay of the Total Ion Chromatogram for the Four Carbonated Beverages Indicating the Additional Peaks Observed with the Static Headspace Method.

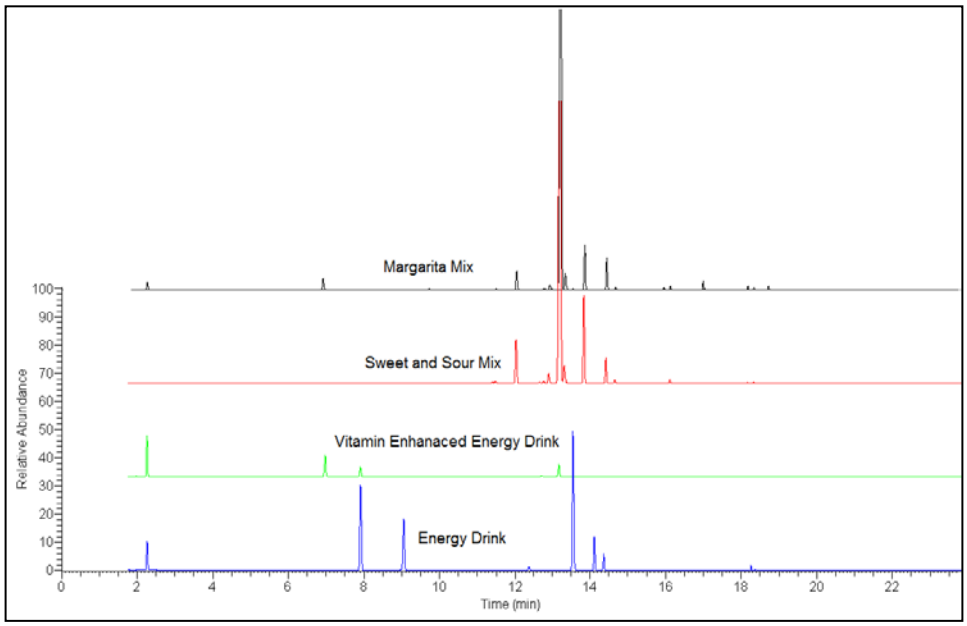

Figure 4: Overlay of the Total Ion Chromatogram for the Two Energy Beverages and Two Cocktail Mixes Indicating the Additional Peaks Observed with the Static Headspace Method.

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Conclusions

The calibration curve data from 0.050 to 20 ppb was excellent. The ability to detect ppt levels of benzene with this instrument at the 0.05 ppb level greatly exceeds current benzene detection level requirements for drinking water (1 ppb for European communities and 5 ppb for the United States).

All eight beverage samples tested contained <1 ppb benzene. The energy drink sample was found to contain 0.065 ppb benzene, indicating the ability of the HT3 to deliver quantitative data well below the 0.5 ppb detection limit of current methods. Furthermore, the detection of additional volatile compounds observed in this static headspace method can greatly assist beverage laboratories in ensuring superior quality levels.

References

1. ICBA Guidance Document to Mitigate the Potential for Benzene Formation in Beverages, First Update 22 June 2006, The British Soft Drinks Association Ltd, London WC2B 5LR
2. Determination of Benzene in Soft Drinks and Other Beverages, May 19, 2006, US Food and Drug Administration, http://www.fda.gov/Food/FoodborneIllnessContaminants/ChemicalContaminants/ucm055179.htm
3. Achieving ppt Levels of Environmental Volatiles with the HT3 Headspace Autosampler, Teledyne Tekmar Application Note, July 2013, www.teledynetekmar.com
4. NIST MS Search 2.0, National Institute of Standards and Technology, US Department of Commerce, Gaithersburg, MD

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