APPLICATION NOTE AN108

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

KEY WORDS: Benzene, Headspace, ppb, ppt, Static

INTRODUCTION

Eight commercially available beverage samples were selected for low-level detection of benzene by static headspace analysis. This study will use the SCION Instruments 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.

Figure 1. SCION HT3 Headspace Sampler together with the SCION Instruments 8300 GC platform in combination with to 8700 SQ-MS equipped with 8400PRO autosampler .

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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 and the US FDA.

A recent Tekmar application note 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 1.

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.

Table 1. Instrumentation operating conditions.

Injector	Split 30:1, 200 °C
Column	Rtx-502.2
Oven Program	60°C (2 min), 8°C/min to 150°C, 20°C/min to 260°C (5 min)
Carrier	Helium
Flow	1.0 ml/min
Autosampler	8400PRO
Software	Compass CDS/ MSWS/ HT3 Teklink
MS transfer line temperature	220°C
Ion source temperature	230°C
Ionization mode	EI
Scan start	1.75
Scan mode	Full Scan/SIM
HT3	Static Value
Oven temperature	120°C
Transfer line temperature	120°C
Sample temperature	70°C
Sample equilibrium	10 min

CALIBRATION CURVES AND DATA

The standards and blanks were analyzed with the HT3 and GC/MS parameters listed in Table 1. Figure 2 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 3 is a head to tail comparison of the reference spectra for benzene to benzene-d6 from the NIST 2.0 library.

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

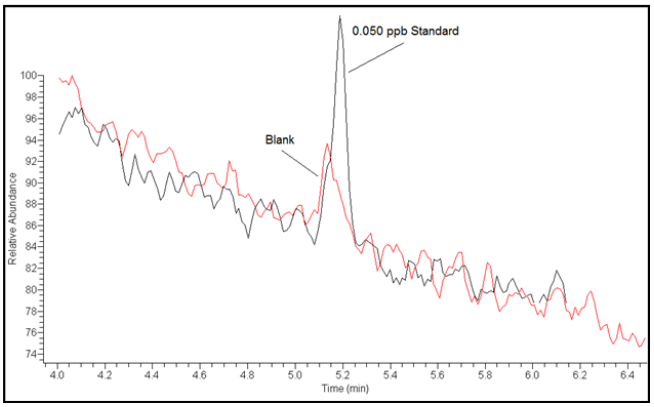

Figure 2. Comparison of the SIM Chromatogram Mass 78 m/z for Blank Water and the 0.050 ppb Standard, Both with Internal Standard.

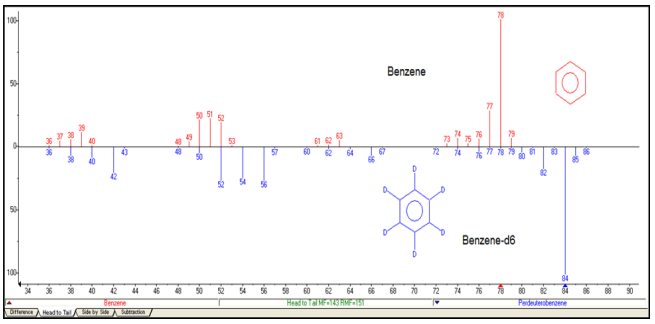

Figure 3. Head to Tail Comparison of Benzene to Benzene-d6.

Table 2 lists the response factor and linear calibration curve data for the 0.050 to 20 ppb benzene standards.

Table 2. Calculated data for benzene

Compound	Rf %RSD 0.050 ppb to 20 ppb	Linearity r^2
Benzene	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 3.

Table 3. 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

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.

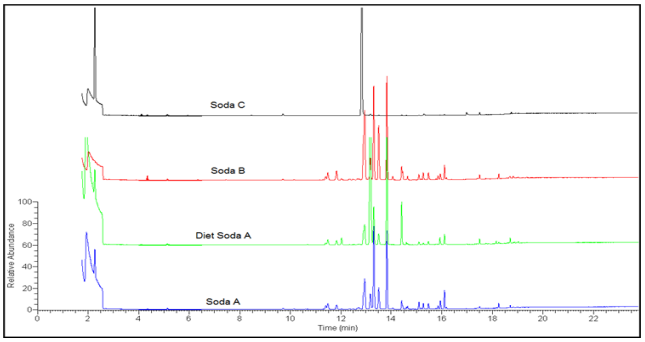

Figure 4. Overlay of the Total Ion Chromatogram for the Four Carbonated Beverages Indicating the Additional Peaks Observed with the Static Headspace Method.

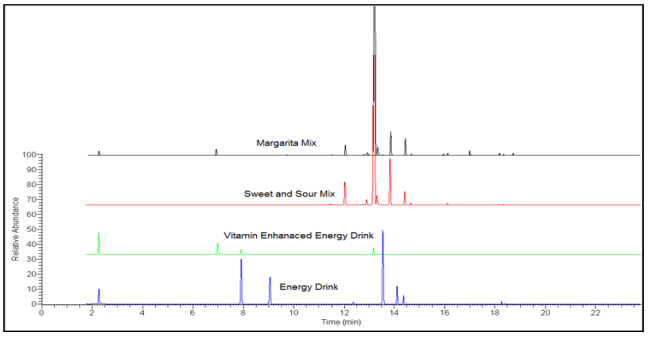

Figure 5. Overlay of the Total Ion Chromatogram for the Two Energy Beverages and Two Cocktail Mixes Indicating the Additional Peaks Observed with the Static Headspace Method.

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

CONCLUSION

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.

ORDER INFORMATION

Part number	SCION HT3 Headspace
SC149300000	**HT3 Headspace Autosampler 110 V.** This static headspace autosampler comes with our 60 position autosampler, 10 position platen heater, integrated Optimix equilibrium system, and completely heated Silcosteel sample pathway. Entire system can be heated from ambient up to 300C in increments of 1C. Valve and loop configuration includes 1ml standard loop. System's gas flows and pressure are electronically monitored and controlled. Windows XP or 2000 is required to operated the included HT3 TekLink software. Power requirements are 115V, 50/60 Hz, 10A. Make sure to order the appropriate GC interface cable to ensure proper installation.
SC149300100	**HT3 Headspace Autosampler 230 V.** This static headspace autosampler comes with our 60 position autosampler, 10 position platen heater, integrated Optimix equilibrium system, and completely heated Silcosteel sample pathway. Entire system can be heated from ambient up to 300C in increments of 1C. Valve and loop configuration includes 1ml standard loop. System's gas flows and pressure are electronically monitored and controlled. Windows XP or 2000 is required to operated the included HT3 TekLink software. Power requirements are 230V, 50/60 Hz, 10A. Make sure to order the appropriate GC interface cable to ensure proper installation.
SC14930000S	**HT3 Dynamic Headspace Autosampler 110V.** This dynamic headspace autosampler comes with our 60 position autosampler, 10 position platen heater, integrated Optimix equilibrium system, and completely heated Silcosteel sample pathway. Entire system, including trap, can be heated from ambient up to 300C in increments of 1C. Valve and loop configuration includes 1ml standard loop. Dynamic mode includes 12" x 1/8" Tenax/Silica Gel and Charcoal (#3) trap and Vocarb 3000 (K) trap. Static and Dynamic modes may be used interchangeably throughout the same schedule. System's gas flows and pressure are electronically monitored and controlled. Windows XP or 2000 is required to operate the included HT3 TekLink software. Power requirements are 115V, 50/60 Hz, 10A. Make sure to order the appropriate GC interface cable to ensure proper installation.
SC14930010S	**HT3 Dynamic Headspace Autosampler 230V.** This dynamic headspace autosampler comes with our 60 position autosampler, 10 position platen heater, integrated Optimix equilibrium system, and completely heated Silcosteel sample pathway. Entire system, including trap, can be heated from ambient up to 300C in increments of 1C. Valve and loop configuration includes 1ml standard loop. Dynamic mode includes 12" x 1/8" Tenax/Silica Gel and Charcoal (#3) trap and Vocarb 3000 (K) trap. Static and Dynamic modes may be used interchangeably throughout the same schedule. System's gas flows and pressure are electronically monitored and controlled. Windows XP or 2000 is required to operate the included HT3 TekLink software. Power requirements are 230V, 50/60 Hz, 10A. Make sure to order the appropriate GC interface cable to ensure proper installation.

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Part number	SCION VERSA Headspace
SC150800100	**Versa Static Headspace Vial Sampler 110V.** This analyzer comes with a 20 position autosampler, single-position platen heater, integrated mixing system, and completely heated inert sample pathway. Entire system can be heated from ambient up to 200 degrees C in increments of 1 degree C. Valve and loop configuration includes 1mL standard loop. Built-in pressure control assures consistent volume regardless of external conditions. Windows XP or higher is required to operate and includes the Versa TekLink 2G software. Power requirements are 115V, 50/60 Hz, 5A. Make sure to order the appropriate GC interface cable to ensure proper installation.
SC150800200	**Versa Static Headspace Vial Sampler 230V.** This analyzer comes with a 20 position autosampler, single-position platen heater, integrated mixing system, and completely heated inert sample pathway. Entire system can be heated from ambient up to 200 degrees C in increments of 1 degree C. Valve and loop configuration includes 1mL standard loop. Built-in pressure control assures consistent volume regardless of external conditions. Windows XP or higher is required to operate and includes the Versa TekLink 2G software. Power requirements are 230V, 50/60 Hz, 5A. Make sure to order the appropriate GC interface cable to ensure proper installation.

SCION Instruments

UK
4 Michaelson Square
Livingston
EH54 7DP, Scotland, UK
Phone +44 1506 300 200
sales-eu@scioninstruments.com

The Netherlands
Amundsenweg 22-24
4462 GP Goes,
The Netherlands
Phone +31 (0) 113 287 600
sales-eu@scioninstruments.com