Trace Level Headspace Analysis of Benzene in Beverage Samples

Keywords

Dynamic Headspace
Dynamic Sweeping
Adsorbent Trapping
Trace Detection
Benzene
Consumer Beverage
Dual Needle
FDA
EPA
VOC

For over 17 years, EST has specialized in analytical instrumentation. EST is both a manufacturer and national distributor for several European companies. It is our goal to provide our customers with reliable, cost effective and highly automated products designed to reduce cost and increase profitability to give their businesses an advantage. In order to ensure your success and keep your business, we back everything we sell with superior service and support.

Introduction

Static Headspace systems offer a simple and robust method of introducing volatile organic compounds into a GC. However, one of the drawbacks of static headspace analysis is that the technique cannot provide the sensitivity necessary to detect compounds at trace levels since only a portion of the equilibrated headspace vapor is injected. Trace detection analysis generally requires much larger volumes of headspace vapor and the ability to pre-concentrate the compounds prior to GC analysis.

Therefore the ability to perform trace level headspace analysis has historically been limited to purge and trap. ***Until NOW!***

A new multi-functional headspace system with integrated adsorbent trapping capabilities has been developed for VOC determination at unprecedented part per trillion (ppt) levels of detection.

Discussion

The **Markelov HS9000** Static and Dynamic Headspace system utilizes a patented sampling needle which is comprised of two passages as shown in *Figure 1*.

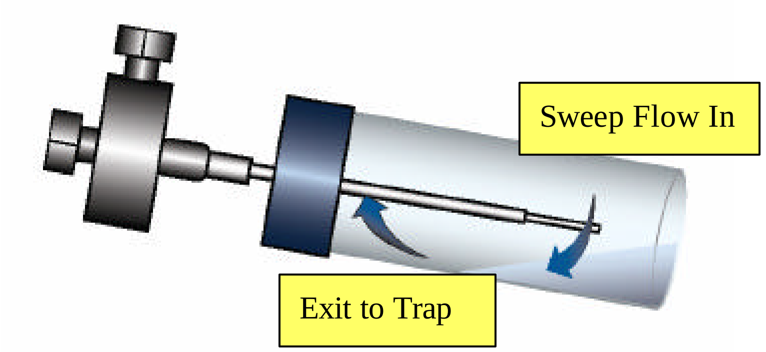


Figure 1: Dual Passage Needle

This dual passage needle (needle within a needle) delivers the ability to concentrate the compounds contained in the vapor phase onto the integrated adsorbent trap by continuously sweeping and displacing the headspace above the sample contained in the sealed vial as shown in *Figure 2*. After the adsorbent trap has been loaded it is then heated and back-flushed to transport the compounds to the GC as shown in *Figure 3*.

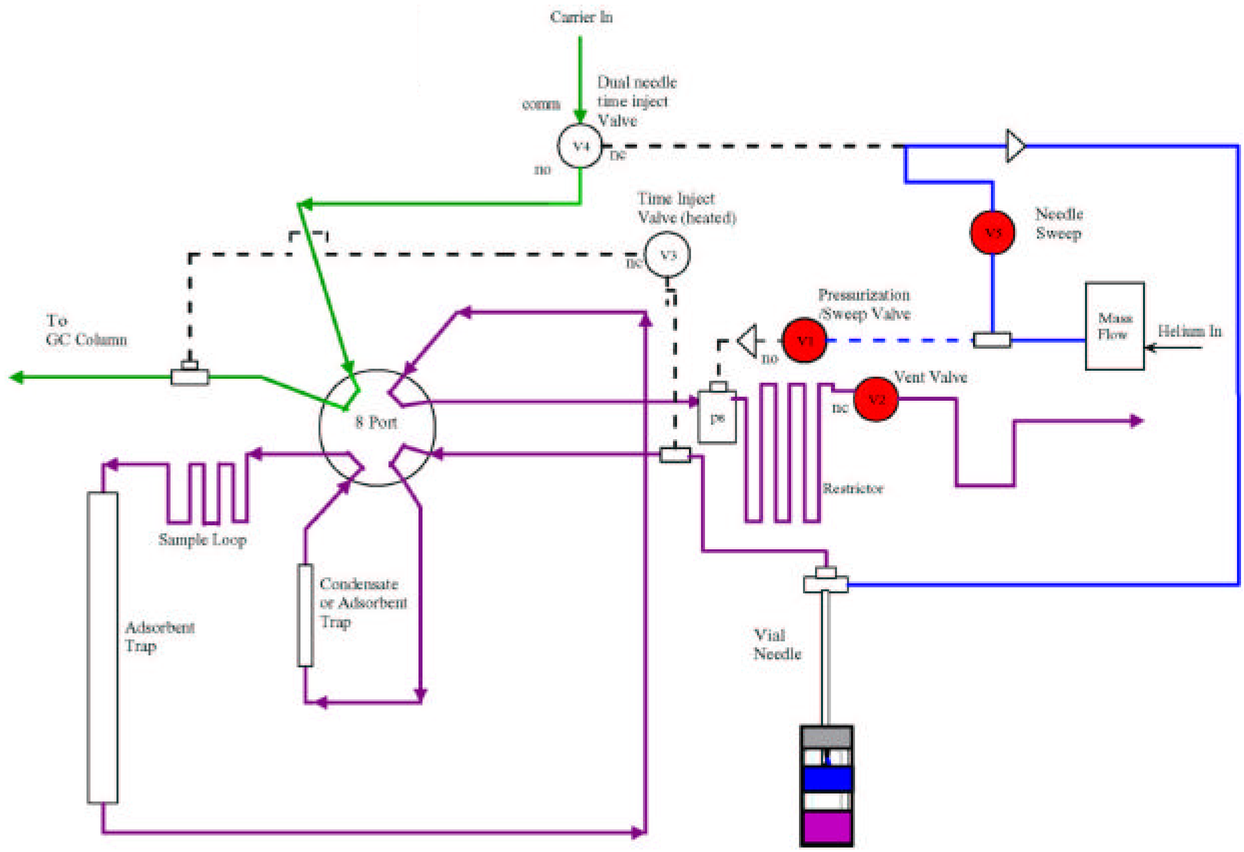


Figure 2 – HS9000 Dynamic Sweep Mode

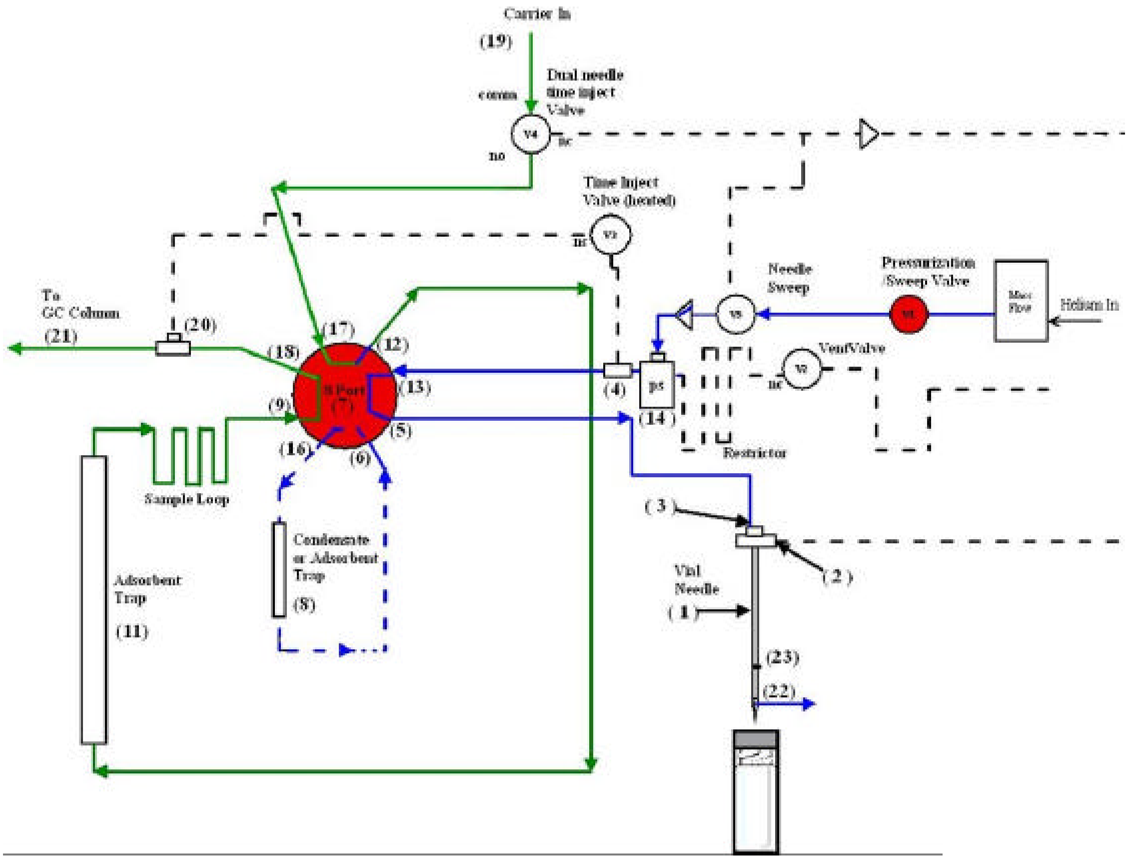
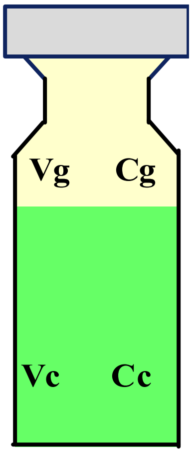


Figure 3 – Trap Inject Mode (Desorb)

By incorporating the trapping technology and dual passage needle, the HS9000 is capable of collecting the entire volume of equilibrated headspace vapor for analysis. The sensitivity of headspace analysis is now proportional to the total mass of a compound in the vapor phase at equilibrium with the sample as illustrated in *Figure 4*. Purge and Trap levels of sensitivity can be achieved while maintaining the time tested principles of Equilibrium Headspace (Static) analysis.



Dynamic Sweeping:

$$Mg = VgCo/\,(K + Vg/Vc)$$

C_o = Initial concentration of analyte in the sample
C_c = Concentration in matrix
C_g = Concentration in gas phase (headspace)
V_c = Volume of sample matrix
V_g = Volume of gas (headspace) above sample
K = Partition coefficient = C_s/C_g
V_g/V_c = Phase Ratio (ß)
Mg = mass of analyte in sampling volume

Figure 4: Dynamic Headspace Illustration

Experimental Results

Beverages which contain ascorbic acid (Vitamin C) have the potential to form benzene under certain conditions through the decarboxylation of benzoic acid. Therefore the requirement to test consumer beverages for the presence of benzene exists to assure that levels are below the safe maximum contaminate level. To achieve the required low level of detection for benzene, testing laboratories normally analyze samples by the use of a purge and trap (P&T) method or a static headspace (HS) method with single ion monitoring (SIM). Purge and Trap methods can deliver the required sensitivity however the problem of foaming the sample into the analytical instrument causing erroneous results is a major concern especially when analyzing juices or other carbonated beverages. Moisture introduction into the GC/MS is also a concern associated with the purge and trap method.

To demonstrate the Markelov HS9000 static and dynamic headspace analyzer's ability to concentrate the compounds prior to injection, the determination of benzene in beverages at ppt levels without the use of single ion monitoring will be presented.

The linear range of the system was first established by analyzing a six-point calibration curve (0.2 ppb – 20 ppb). The R^2 value as shown in *Figure 5* was calculated to be 0.9998.

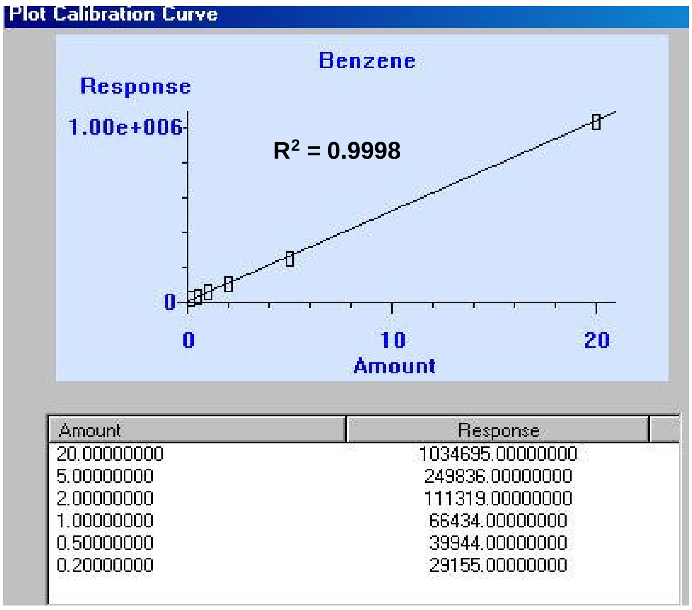


Figure 5 – Calibration data 0.2 ppb – 20 ppb

The precision of the method was determined by analyzing four samples spiked at 5 ppb and four spiked samples at 0.5 ppb. The precision is expressed as %RSD and was calculated to be 2.6% and 1.9% respectively as shown in *Figures 6 and 7*.

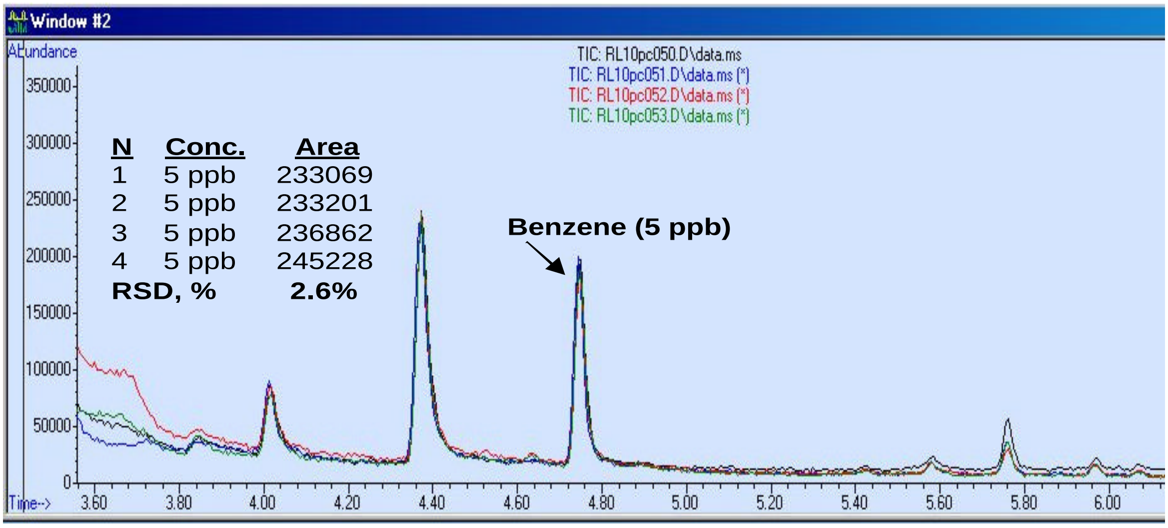


Figure 6 – Precision data of beverage sample spiked with 5 ppb Benzene

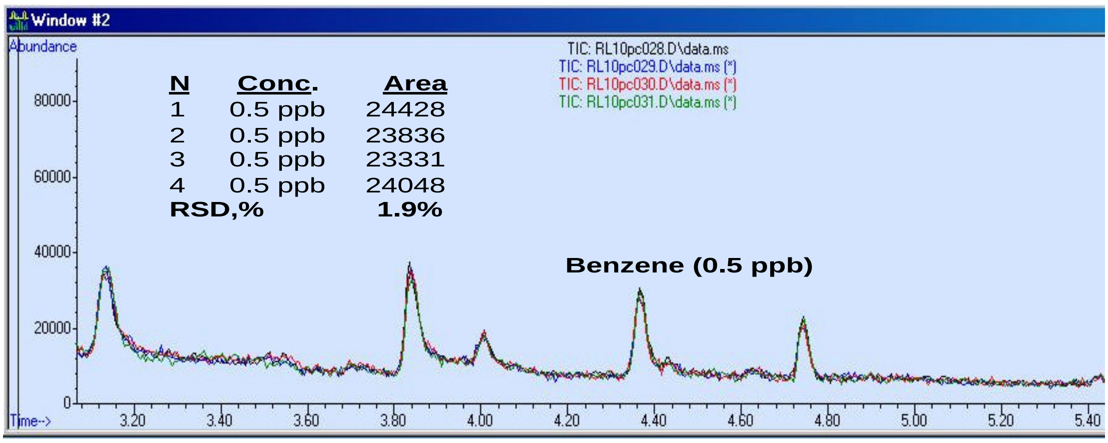


Figure 7 – Precision data of beverage sample spiked with 0.5 ppb Benzene

All the samples were analyzed utilizing the HS9000 parameters listed in *Figure 8*. The sweep time and sweep flow parameters were selected to displace the headspace volume by a factor of 2 to ensure that the entire equilibrated headspace vapor is concentrated. A volume of 30 milliliters was used in this work. These parameters were also carefully selected to ensure there was no additional migration of benzene from the sample into the headspace during the sweeping process.

Headspace	Markelov HS 9000
Trap Type	Vocarb 3000- Type "K" Carbopack B Carboxen 1000 Carboxen 1001
Sample Vial Temperature	70º C
Sample Size	5 milliliters
Sample Equilibration Time	15.0 minutes
Mixing	Horizontal Rotary- low speed
Sample Mode	Adsorbent Trap
Trap Ready Temperature	35º C
Moisture Reduction Pre-Trap	Ambient
Sweep Flow Rate	60 ml/min
Sweep Time	30 seconds
Dry Sweep	2 minutes at 40 ml/min
Trap Inject (Desorb)	260º C for 1.0 minutes
Trap Bake Temperature	270º C for 8 minutes
Trap Bake Flow Rate	120 ml/min

Figure 8 – Markelov HS9000 parameters

The 'Dry Sweep' mode, and the Pre-trap moisture management techniques were also employed to minimize the amount of moisture transferred to the GC/MS. Dry Sweep is the mode which directs inert gas over the adsorbent trap after the trap has been loaded with the sample and before the injection to the GC. The Pre-trap as previously shown in *Figure 2* is used as a condensation trap (cool zone) to remove the moisture from the sample vapor before the adsorbent trap.

Other Markelov HS9000 modes of sample introduction which can provide part per trillion level of detection include:

Dynamic sweeping with concentration at the GC Inlet (2N on Column)
The dual passage needle introduces the GC carrier gas to the sealed sample vial to continuously sweep and displace the headspace above the sample to concentrate the sample vapors at the GC Inlet.

Multiple Headspace Extractions concentrated onto the adsorbent trap (MHE – Trap)
Multiple injections from a single sample vial are concentrated on the adsorbent trap before introduction to the GC.

Multiple Headspace Extractions concentrated at the GC inlet (MHE-GC)
Multiple injections from a single sample vial are concentrated at the GC inlet before analysis.

Bulk Sampling
Multiple sample vials analyzed with identical conditions can be concentrated on the adsorbent trap before a single injection to the GC.

Conclusion

The Markelov HS9000 *Static and Dynamic Headspace System* has been demonstrated to deliver classical purge and trap performance in terms of sensitivity while still adhering to the time tested principles of equilibrium headspace. All the benefits of a traditional static headspace system and a purge and trap system have been incorporated into a single multi-functional sample introduction instrument ideal for any testing laboratory. Other analytical advantages include the patented horizontal rotary mixing technique, electronic flow and pressure control, temperature control beyond 300^0C and inert sample pathways.

With courtesy of EST ANALYTICAL ©

Headquarters
JSB International
Tramstraat 15
5611 CM Eindhoven
T +31 (0) 40 251 47 53
F +31 (0) 40 251 47 58

Zoex Europe
Tramstraat 15
5611 CM Eindhoven
T +31 (0) 40 257 39 72
F +31 (0) 40 251 47 58

Sales and Service

Netherlands
Apolloweg 2B
8239 DA Lelystad
T +31 (0) 320 87 00 18
F +31 (0) 320 87 00 19

Belgium
Grensstraat 7
Box 3 1831 Diegem
T +32 (0) 2 721 92 11
F +32 (0) 2 720 76 22

Germany
Max-Planck-Strasse 4
D-47475 Kamp-Lintfort
T +49 (0) 28 42 9280 799
F +49 (0) 28 42 9732 638

UK & Ireland
Cedar Court,
Grove Park Business Est.
White Waltham, Maidenhead
Berks, SL6 3LW
T +44 (0) 16 288 220 48
F +44 (0) 70 394 006 78

info@go-jsb.com
www.go-jsb.com

jsb