Trace Level Headspace Analysis of Benzene in Beverage Samples

Introduction:

Beverages which contain ascorbic acid (Vitamin C) have the potential to form benzene under certain conditions through the decarboxylation of benzoic acid. Therefore, these beverages need to be tested for the presence of benzene and to assure that benzene levels are below the maximum contaminate level. To achieve the required low level detection of 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. This paper will discuss a third alternative, utilizing the Dynamic Headspace option of the Markelov HS9000 in order to determine trace amount of benzene in beverage samples.

Discussion:

Static Headspace systems offer a simple and robust method of introducing volatile organic compounds to 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 can be injected. Trace detection analysis generally requires much larger volumes of headspace vapor and the ability to pre-concentrate these compounds of interest prior to GC analysis.

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

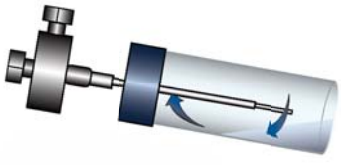


Figure 1: Dual Passage Needle

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. After the adsorbent trap has been loaded it is then heated and back-flushed in order to transport the compounds to the GC. The analytical advantages of a static headspace system equipped with a dual sampling needle capable of dynamically sweeping the headspace and concentrating the compounds prior to injection will be demonstrated by presenting sub ppb level results of Benzene in a beverage sample.

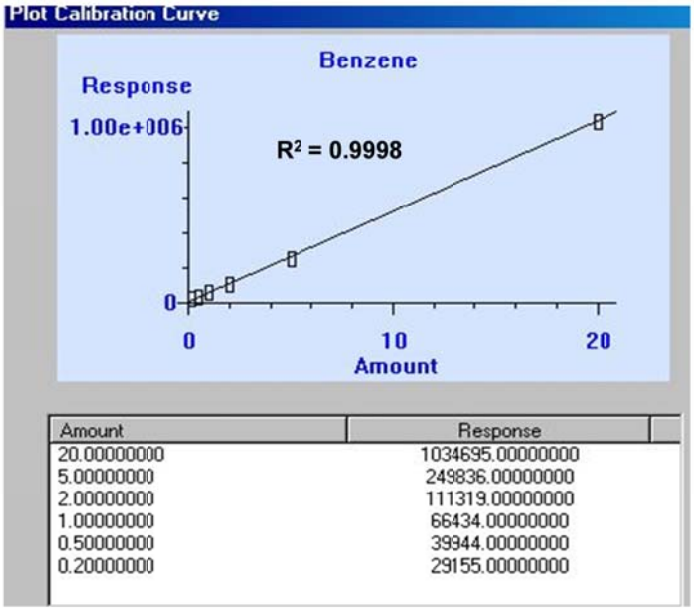
Experimental:

The Markelov HS9000 in dynamic mode was the sampling system utilized for this experiment. The headspace system was equipped with a Vocarb 3000 (K) trap. The sweep time and sweep flow parameters were selected to displace the headspace volume by a factor of 2 in order to ensure that the entire equilibrated headspace vapor is concentrated. A volume of 30 milliliters was used for this analysis. 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. The HS9000 parameters are listed in Table 1.

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

Table 1: HS9000 Parameters

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 2 was calculated to be 0.9998.



Amount	Response
20.00000000	1034695.00000000
5.00000000	249836.00000000
2.00000000	111319.00000000
1.00000000	66434.00000000
0.50000000	39944.00000000
0.20000000	29155.00000000

Figure 2 – 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 3 and 4.

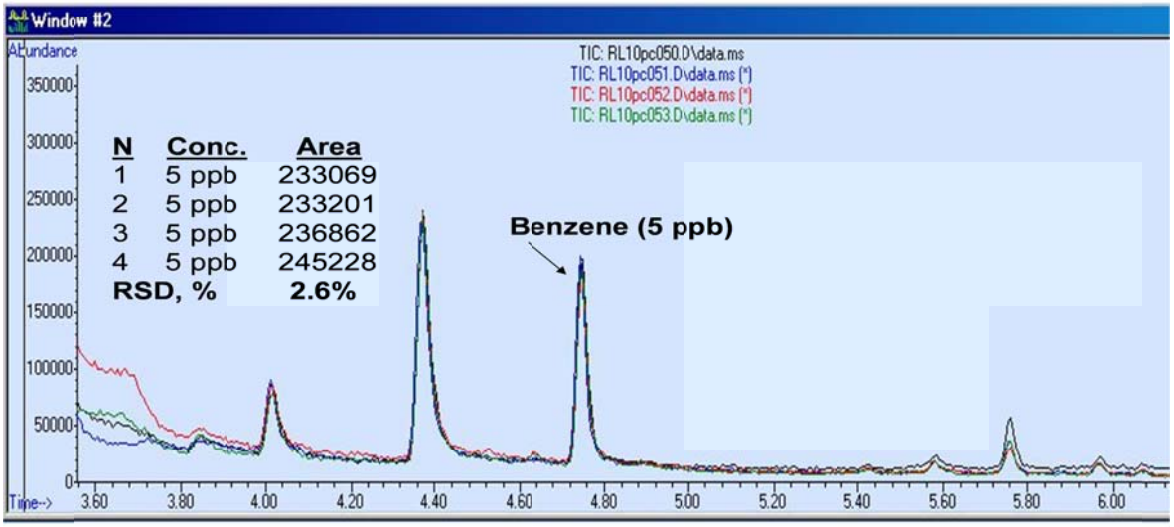


Figure 3 – Precision data of beverage sample spiked with 5 ppb Benzene

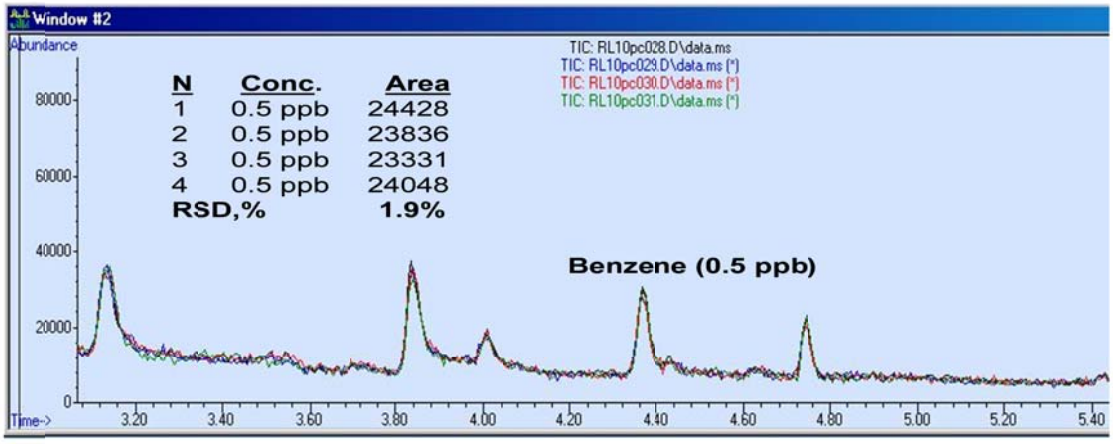


Figure 4 – Precision data of beverage sample spiked with 0.5 ppb Benzene

Conclusion:

The results of this study demonstrate the ability of the Markelov HS9000 Static and Dynamic Headspace to sample Benzene at sub ppb levels. The Markelov HS9000 has all the benefits of a traditional static headspace system and a purge and trap system 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, three different types of sampling methods, and inert sample pathways.