

**GERSTEL**

AppNote 7/2008

Automated Dynamic Headspace Sampling of Aqueous Samples using Replaceable Adsorbent Traps, Part II

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KEYWORDS

Dynamic Headspace, Gas Chromatography, Replaceable Traps

ABSTRACT

Static (equilibrium) headspace sampling is commonly used for GC determination of volatiles in solid and liquid samples. Since this technique relies on the analyte partitioning between the sample and headspace and uses a small injection volume it may not provide adequate detection limits, particularly for higher molecular weight, higher boiling analytes and for polar analytes in aqueous samples.

In this study we describe the use of an automated dynamic headspace sampler for determination of volatiles in aqueous samples. This sampler uses a two-needle design to flush the headspace of standard headspace vials onto replaceable adsorbent traps that can be thermostatted to optimize analyte recovery and control interference from water vapor. Following analyte transfer, the adsorbent traps can be automatically dry purged to further eliminate water before introduction into the integrated thermal desorber. This design enables automated optimization of trapping conditions including choice of adsorbent, and has the potential for automated internal standard addition and automated calibration.

To illustrate the versatility of the DHS system, examples of the determination of trace levels of volatile organic compounds (VOCs) in aqueous samples are shown. Detection limits and linearity are discussed in the following. In a previous

Application Note 4/2008, optimization of parameters required for dynamic headspace analysis of aqueous samples was performed and results from several other sample types were presented as examples

INTRODUCTION

The GERSTEL Dynamic Headspace System (DHS) (Figure 1) is an accessory for the MultiPurpose Sampler (MPS 2). The DHS technique enables dynamic purging of the headspace above a sample. Analytes in the purged headspace are trapped onto a 2 cm adsorbent bed in a compact glass tube. The tube is then placed into the Thermal Desorption Unit (TDU) and the analytes thermally desorbed and introduced to the gas chromatograph. Desorbed analytes are cryofocused in the Cooled Injection System (CIS 4) inlet to improve peak shape and increase sensitivity.

Figure 2 shows a schematic of the trapping and desorption process.



Figure 1. GERSTEL MPS 2 / DHS on an Agilent Technologies 7890 GC.

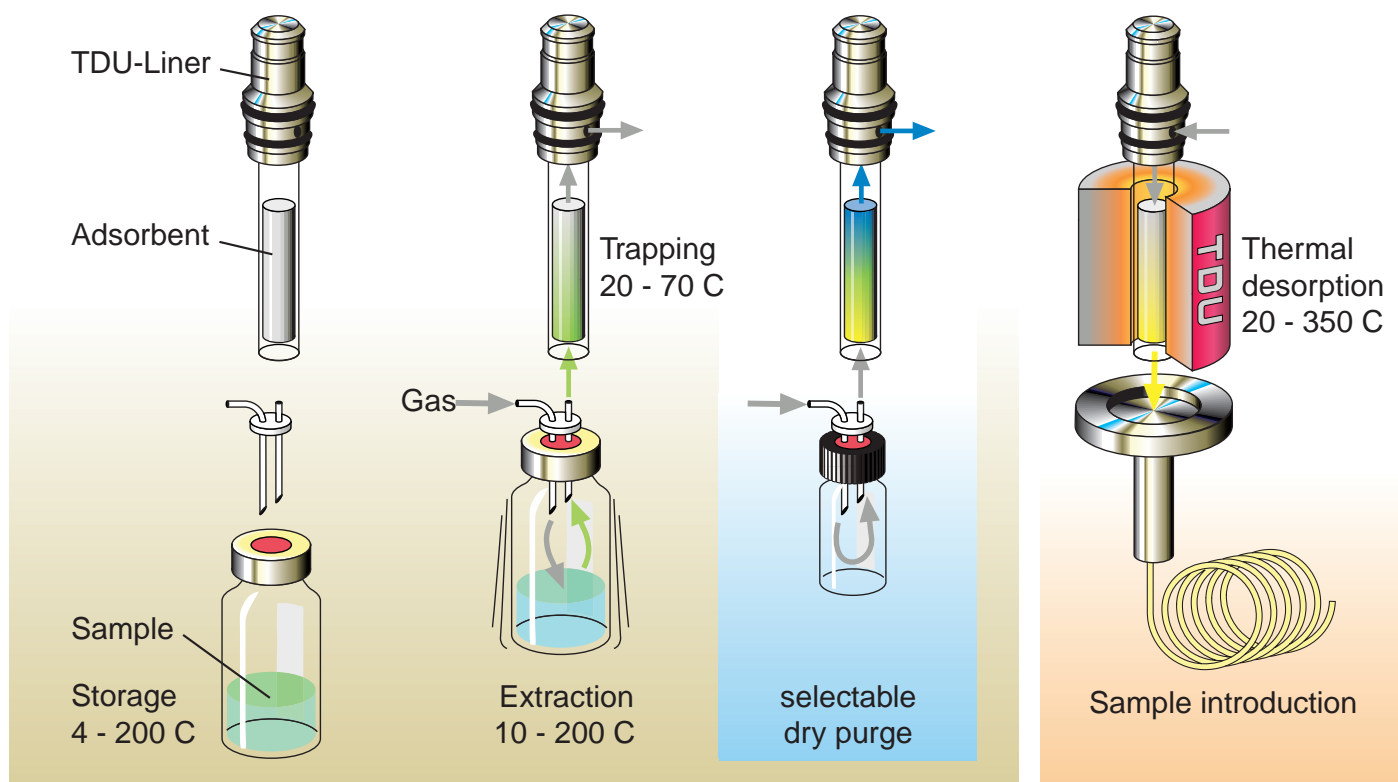


Figure 2. Schematic view of DHS process.

Aqueous and high water content samples can often be problematic for headspace analysis. The presence of water vapor in the headspace above the sample can lead to poor precision. The increased sensitivity achieved through agitation and dynamic purging of the sample in the GERSTEL DHS allows the analysis to be carried out at lower temperatures, thereby reducing the amount of water in the headspace. Water can also be managed using a dry purge function in the DHS, used to purge humidity out of the adsorbent trap, and by using the solvent vent function in the TDU.

This study examines the determination of volatile organic compounds (VOCs) in aqueous samples using dynamic headspace. The analysis of an EPA Method 640 Volatiles mix in salt solutions and benzene in cola are shown as examples. In Application Note 4/2008, the optimization of dynamic headspace analysis for aqueous samples was examined and several sample types were analyzed.

EXPERIMENTAL

Optimized analysis conditions.

Trap: Carbopack X/Carboxen 569
DHS: 30°C trap temperature
35°C incubation temperature
150 mL purge volume
30 mL/min purge flow
TDU: splitless
40°C (0.2 min); 720°C/min;
325°C (2.5 min)
PTV: 0.2 min solvent vent (50 mL/min)
glass bead liner; split 10:1
-150°C (0.2 min); 12°C/s;
280°C (3 min)
Column: 20 m Rtx-624 (Restek)
 $d_i = 0.18 \text{ mm}$ $d_f = 1.0 \text{ }\mu\text{m}$
Pneumatics: He, ramped pressure
19.6 psi (2 min); 1.36 psi/min;
38.6 psi (5 min)
Oven: 35°C (4 min); 15°C/min; 200°C
MSD: Scan, 15 - 350 amu

Sample Preparation. Benzene and d_6 -benzene standards were prepared in methanol. Five grams of water or cola sample were weighed into a 20 mL screw capped vial.

RESULTS AND DISCUSSION

Benzene is a carcinogen which can form in some beverages containing benzoate salts (which are used as antimicrobials) in combination with ascorbic acid [1]. Benzene can form when these products are subjected to heat or light. Standard analysis methods for the determination of benzene in such products rely on static headspace analysis. When using static headspace, the sample must be heated to 60-75°C in order to drive benzene into the headspace of the vial to such a degree that adequate sensitivity is reached. Higher sample temperatures invariably lead to the introduction of more water into the analysis system, which can negatively impact the quality of results. In the work reported here, the DHS technique was used. Since DHS is a much more sensitive analysis technique than static headspace, the analysis can be performed at lower temperatures. In this example, a five gram aliquot of sample or standard was equilibrated for 5 minutes at 35°C. The sample/standard was then extracted for 5 minutes at 30 mL/min for a total volume of 150 mL. The analyte and internal standard were collected on a trap filled with Carbopack X and Carboxen 569. Deuterated benzene was added as an internal standard at a level of 10 ng/mL. A six point external calibration curve was established using water as a matrix.

Figure 3 shows the resulting calibration curve for benzene over the range 0.5-20 ng/mL. The DHS method shows excellent linearity over this range with a correlation coefficient of 0.9993.

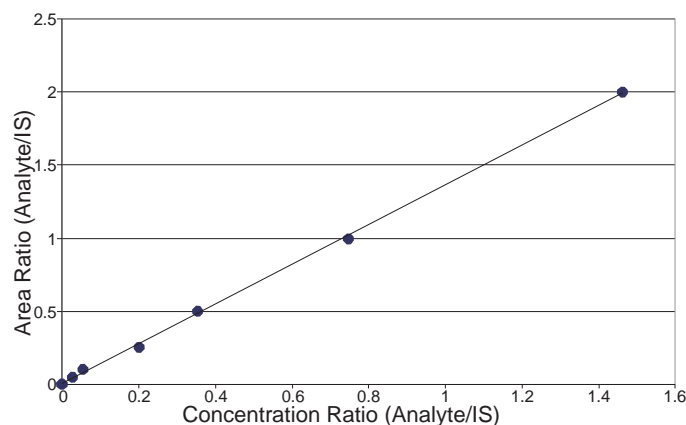


Figure 3. Benzene Calibration Curve.

Figure 4 shows extracted ion chromatograms obtained from the 0.5 ng/mL standard. All data for this analysis was acquired in full scan mode. Three samples of a cola product were spiked with 1 ppb benzene and 10 ppb internal standard. The average calculated value for the three samples was 1.16 ppb with an RSD of 6.6 %. No benzene was found in any of the un-spiked cola samples.

Underground salt domes are thick beds of salt which can be found at great depths. These salt domes can be found among other places in the Gulf Coast region of the United States. Salt domes can be a valuable resource of NaCl. They are typically mined by drilling deep down into the dome, injecting water, which dissolves the salt, and then pumping the resulting brine to the surface. The brine must be analyzed for volatile impurities. This is usually carried out using the purge and trap technique. The results reported here are based on analysis work performed using dynamic headspace (DHS). A solution of 20 % NaCl in water was used as a synthetic matrix for method development. Authentic brine samples were obtained from a commercial source.

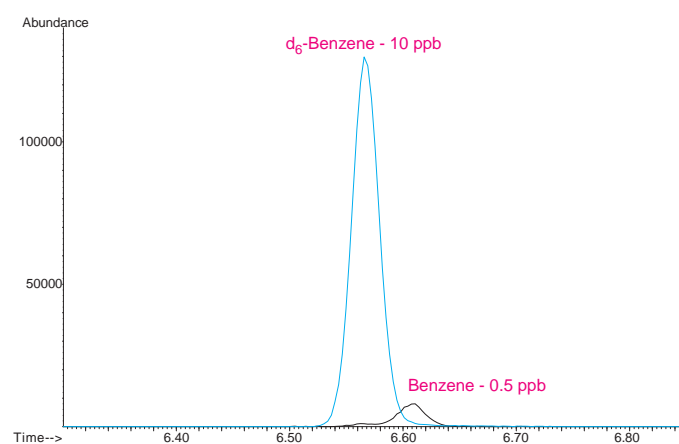


Figure 4. Extracted Ion Chromatograms of d₆-Benzene and Benzene in a Cola Sample.

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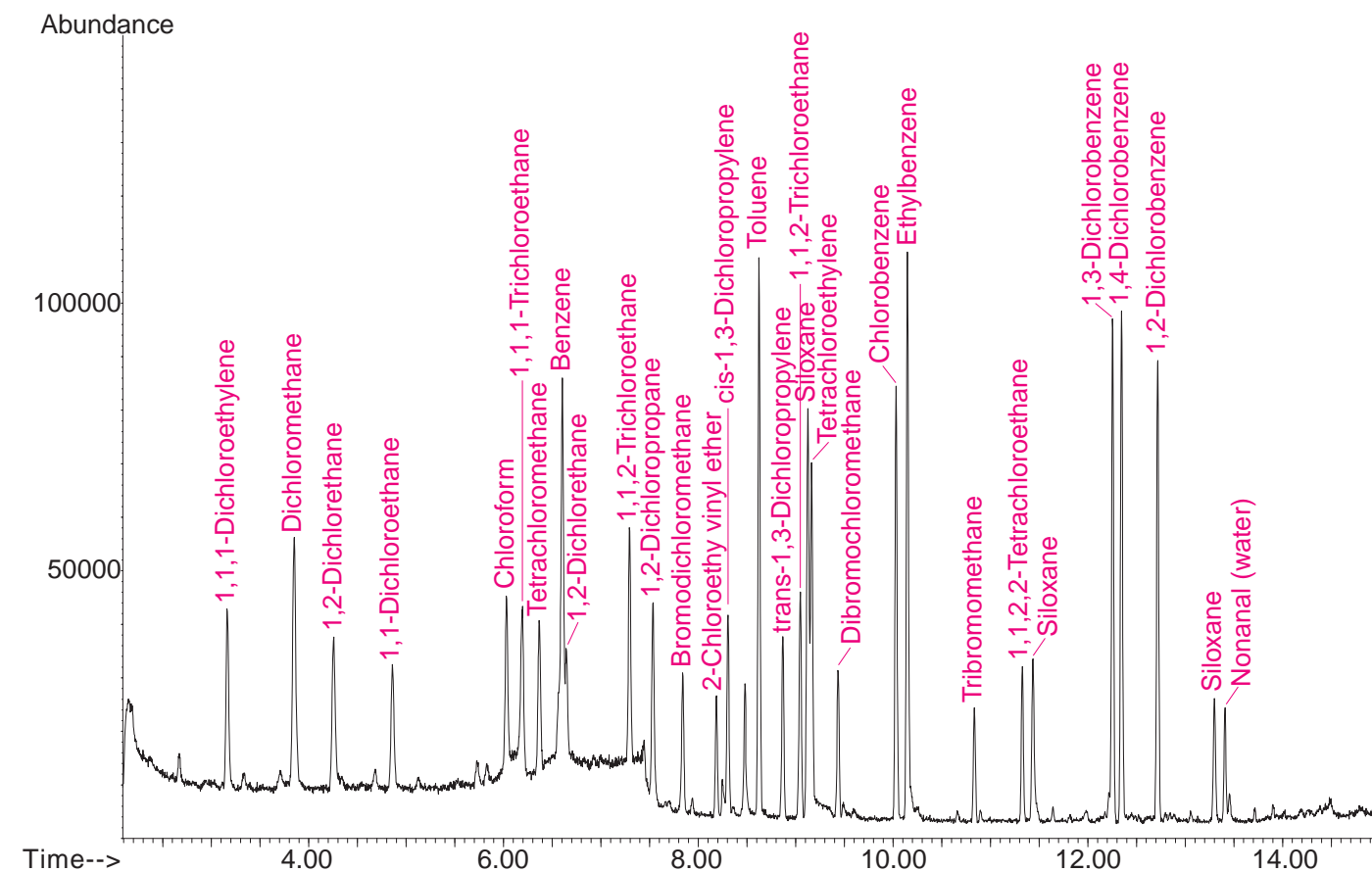


Figure 5. Total Ion Chromatogram of VOC's in Brine Solution.

Figure 5 shows the chromatogram obtained after DHS of a synthetic matrix spiked at a concentration of 2 ppb. All 26 compounds are clearly seen in the total ion chromatogram. The linearity of this analysis is demonstrated in Figure 6, which shows the calibration

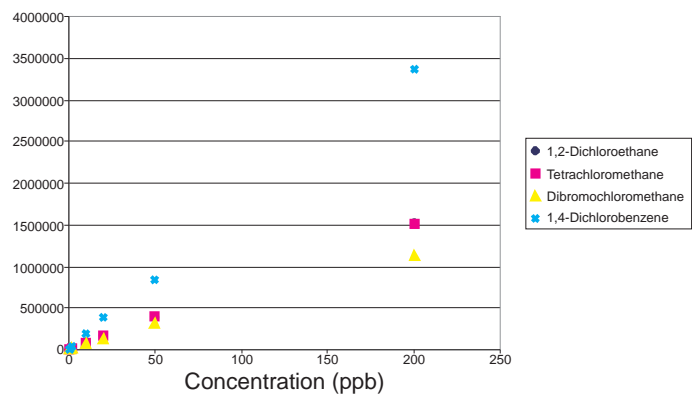


Figure 6. Calibration Curves for 4 of 26 Analytes.

Figure 7 shows the total ion chromatogram resulting from DHS extraction of a brine sample. Several volatile organic solvents and polyhalogenated hydrocarbons are seen in the samples. The largest peak is identified as 1-bromo-2-chloroethane. A 3-point calibration curve was used to determine the concentration levels of benzene in three different brine samples. Table 2 lists the results.

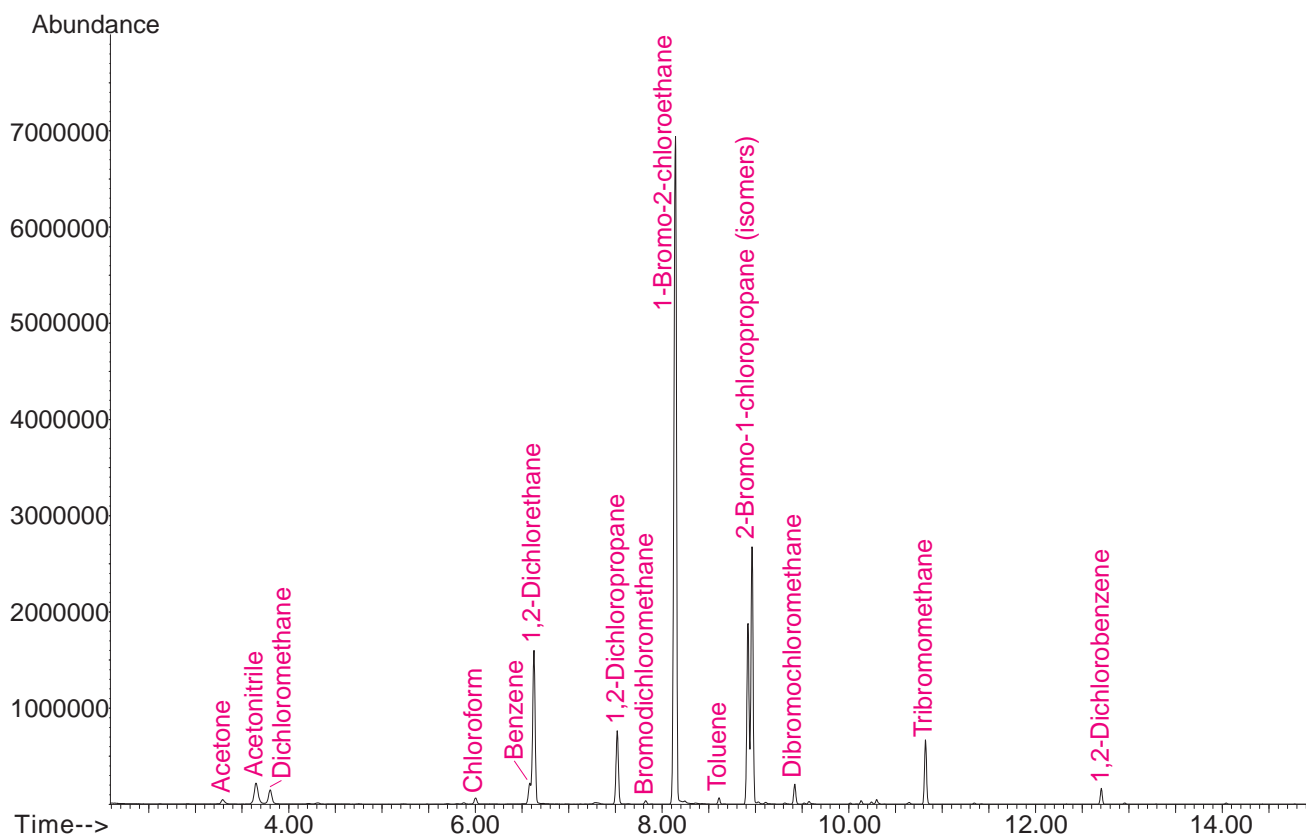


Figure 7. Total Ion Chromatogram from a Brine Sample.

Table 2. Quantitative Results for Benzene in Brine Samples.

Sample	Benzene [ppb]
Sample 1	14
Sample 2	10
Sample 3	2.6

curves for 4 of the 26 analytes over the range from 0.5-200 ppb. Correlation coefficients and RSDs are listed in Table 1. The precision was determined based on 5 injections at a level of 10 ppb. The precision and linearity are both excellent. These four compounds were selected at random as representative of the total 26 analytes.

Table 1. Precision and Linearity Data.

Analyte	Quant Ion [amu]	Correlation Coefficient	RSD (n=5) [%]
1,2-Dichloroethane	61	0.9998	3.43
Tetrachloromethane	117	0.9998	2.63
Dibromochloromethane	129	0.9994	5.14
1,4-Dichlorobenzene	146	0.9998	3.91

CONCLUSIONS

The GERSTEL Dynamic Headspace (DHS) accessory for the MultiPurpose Sampler (MPS 2) adds a highperformance tool to the analyst's toolbox for trace analysis of aqueous and high water content samples. Dynamic Headspace is a concentration technique that provides better sensitivity and lower detection limits than SPME or static headspace. The ability to automatically change traps facilitates method optimization. A wide range of adsorbent materials can be packed into the TDU tubes including customized trapping material or combinations for specific analytes or for best possible water management.

The DHS sample incubation/extraction temperature can be varied from 20-200°C and the trapping temperature from 20-70°C for method optimization. Several options are available for effective water management: The sample temperature can be reduced to reduce water transfer into the trap; the trap temperature can be increased to eliminate condensation; the DHS dry purge can be selected in the method to remove water from the trap following the extraction step; or the solvent vent mode in the TDU can be selected to purge water from the trap prior to thermal desorption. Based on optimized methods, successful examples of the determination of VOCs in a cola drink and in brine were presented. Dynamic headspace analysis provides an alternative to purge and trap for the analysis of brine samples. The PrepAhead function in the Maestro software along with fast GC analysis using the MACH module can be used to reduce cycle times and improve productivity and throughput. One advantage of DHS in comparison with Purge & Trap is the use of replaceable traps. A sample, which may contain high levels of analytes, will not cause the system to shut down due to sample overload.

REFERENCES

- [1] P.J. Nyman, G.W. Diachenko, G.A. Perfetti, T.P. McNeal, M.H. Hiatt, and K.M. Morehouse, J. Agric. Food Chem, 2008, 56, 571-576.

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