

# Determination of Volatile Organic Compounds (VOCs) in Water

## Part 2: Aromatic VOCs

### INTRODUCTION

The present application note continues with the series "Determination of Volatile Organic Compounds (VOCs) in Water". In Part 1 the determination of chlorinated VOCs was covered [1], while this part will be focused on the analysis of aromatic VOCs.

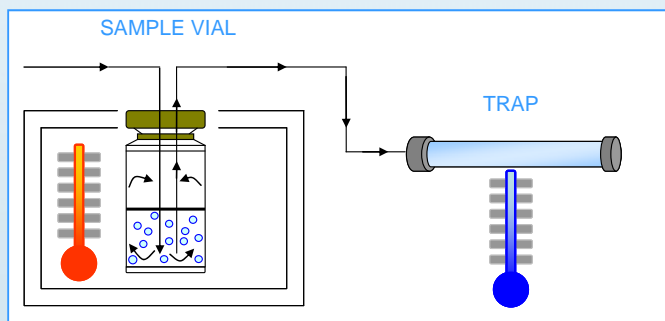
A mixture containing U.S. EPA Method 502.2 targeted aromatic VOCs was analyzed by means of Dynamic Headspace-Gas Chromatography (DHS-GC). As described in Part 1, the headspace sampling system consists of the MASTER DHS Dynamic Head Space Sampler, combined with the MASTER AS Automatic Sampler, operated in "purging mode", according to the above cited EPA method [2]. The extracted VOCs are then analyzed by GC using a Flame Ionization Detector (FID).

The obtained results show that the Dynamic Headspace sampling technique fulfils the requirements for reliable determination of aromatic VOCs in water. Detection limits and calibration results are presented for each standard compound.

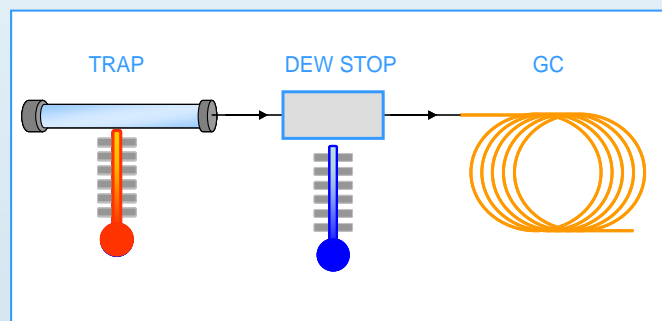
### INSTRUMENTATION

When the MASTER DHS is operated in purging mode, the sample is placed in a sealed vial and thermostatted in a temperature-controlled oven. A precise flow of inert gas is purged into the vial through an original dual-needle, the volatiles are swept from the liquid sample and concentrated in a sorbent packed trap kept at low temperature (see *Figure 1*). The trap is then rapidly heated in backflush and the desorbed analytes are passed through the "Dew Stop" for water removal and introduced directly into the GC system (see *Figure 2*).

In addition, the MASTER DHS combined with the MASTER AS Automatic Sampler allows sample overlapping with constant incubation time, increasing sample capacity, and maximizing vial processing.



*Figure 1. The constant sweeping of the thermostatted sample promotes the enrichment of the volatile compounds on the sorbent trap, therefore resulting in superior sensitivity.*



*Figure 2. The trap is instantaneously desorbed and the volatile compounds are passed through the Dew Stop device which efficiently removes humidity regardless of the analytes.*

## EXPERIMENTAL

### Sample

A volume of 10 mL of a standard solution containing 1 ppb of each compound in water was added to a 20-mL vial. The standard solution was purchased from Supelco (Product No. 47933).

### System configuration and control

DHS and GC-FID conditions are summarized in *Table 1*.

*FID* : The most used GC detection system measures the ions produced by organic compounds during combustion. It is extremely sensitive with a wide dynamic range of seven orders of magnitude.

The Clarity™ Chromatography Station software provides full control of the MASTER DHS and the MASTER GC, data acquisition and processing.

### Calibration

A method calibration covering the entire analytical range for each target analyte was performed. A six-concentration-level calibration curve was plotted. The applied calibration ranges are described in *Table 2*.



*Figure 4. For maximum system completeness the MASTER DHS with MASTER AS is easily hyphenated to the MASTER GC .*



*Figure 3. In combination with the MASTER AS, the MASTER DHS delivers complete automation of standard addition to enhance analytical precision.*

**TABLE 1. DHS-GC-FID EXPERIMENTAL CONDITIONS**

#### MASTER DHS

<b>Sample Volume</b>	10 mL
<b>Trap Material</b>	Tenax/ Carbotrap/Carbosieve
<b>Operating Mode</b>	Purging Mode
<b>Valve Temp.</b>	250 °C
<b>Transfer Line Temp.</b>	250 °C
<b>Incubation Temp.</b>	60 °C
<b>Stripping Time</b>	3 min
<b>Stripping Flow</b>	120 mL/min
<b>Trap Stripping Temp.</b>	-10 °C
<b>Injection Time</b>	3 min
<b>Trap Injection Temp.</b>	295 °C
<b>Dew Stop Temp.</b>	0 °C
<b>Baking Time</b>	10 min
<b>Trap Baking Temp.</b>	300 °C
<b>Dew Stop Baking Temp.</b>	200 °C
<b>Baking Flow</b>	80 mL/min

#### MASTER GC

<b>Column</b>	Vocol (Supelco) 60 m x 0.32 mm, 3 µm
<b>Oven</b>	35 °C (8 min) at 4 °C/min to 240 °C (1 min)
<b>Injector</b>	SL/IN (220 °C)
<b>Carrier Gas Flow (He)</b>	3.5 mL/min (split 1:2)
<b>Detector</b>	FID (250 °C)

## RESULTS

As mentioned earlier, volatile compounds were introduced into the GC system by using the MASTER DHS operated in purging mode. The procedure was carried out in accordance to EPA Method 5030C, which describes the use of Purge and Trap technique for the analysis of VOCs in aqueous samples.

It is worth noting that the applied analytical conditions followed the indications given in EPA Method 502.2, though using a FID instead of a Photo Ionization Detector (PID). The choice to use the FID was merely practical, since this universal detector enables the determination of hydrocarbons that could be present in the sample, while the PID is selective to aromatic compounds.

The chromatogram in *Figure 5* shows the separation obtained for the VOCs mixture; aromatic VOCs are listed in *Table 2*. In addition, calibration curves were prepared using a six points curve model; and the correlation factors (R) are reported in *Table 2*. Method Detectable Limits (MDLs) for the listed target analytes were obtained using identical analytical conditions and calculation modes (refer to *Table 2*).

The constant sweeping of the thermostatted sample followed by the focusing of the volatile compounds on the sorbent packed trap results in unmatched sensitivity.

TABLE 2. COMPOSITION OF THE AROMATIC VOCs MIXTURE.

Compounds	Range (ppb)	R	MDL (ppb)	RSD%
1 Benzene	0.4 - 10	0,9995	0.12	2.0
2 Toluene	0.4 - 10	0,9990	0.12	2.1
3 Ethylbenzene	0.4 - 10	0,9985	0.13	2.6
4 <i>m</i> -Xylene	0.4 - 10	0,9999	0.09	7.9
5 <i>p</i> -Xylene	0.4 - 10	0,9999	0.09	7.9
6 <i>o</i> -Xylene	0.4 - 10	0,9998	0.15	4.0
7 Styrene	0.4 - 10	0,9994	0.16	1.5
8 Isopropylbenzene	0.4 - 10	0,9979	0.25	1.7
9 <i>n</i> -Propylbenzene	0.4 - 10	0,9980	0.25	2.4
10 Bromobenzene	0.4 - 10	0,9994	0.32	0.9
11 1,3,5-Trimethylbenzene	0.4 - 10	0,9989	0.19	0.3
12 2-Chlorotoluene	0.4 - 10	0,9993	0.2	4.7
13 4-Chlorotoluene	0.4 - 10	0,9989	0.2	1.0
14 <i>tert</i> -Butylbenzene	0.4 - 10	0,9989	0.24	1.2
15 1,2,4-Trimethylbenzylene	0.4 - 10	0,9987	0.18	0.5
16 <i>sec</i> -Butylbenzene	0.4 - 10	0,9983	0.3	0.1
17 4-Isopropyltoluene	0.4 - 10	0,9982	0.3	5.0
18 1,3-Dichlorobenzene	0.4 - 10	0,9988	0.4	1.8
19 1,4-Dichlorobenzene	0.4 - 10	0,9989	0.4	1.4
20 <i>n</i> -Butylbenzene	0.4 - 10	0,9967	0.6	2.8
21 1,2-Dichlorobenzene	0.4 - 10	0,9987	0.4	2.9

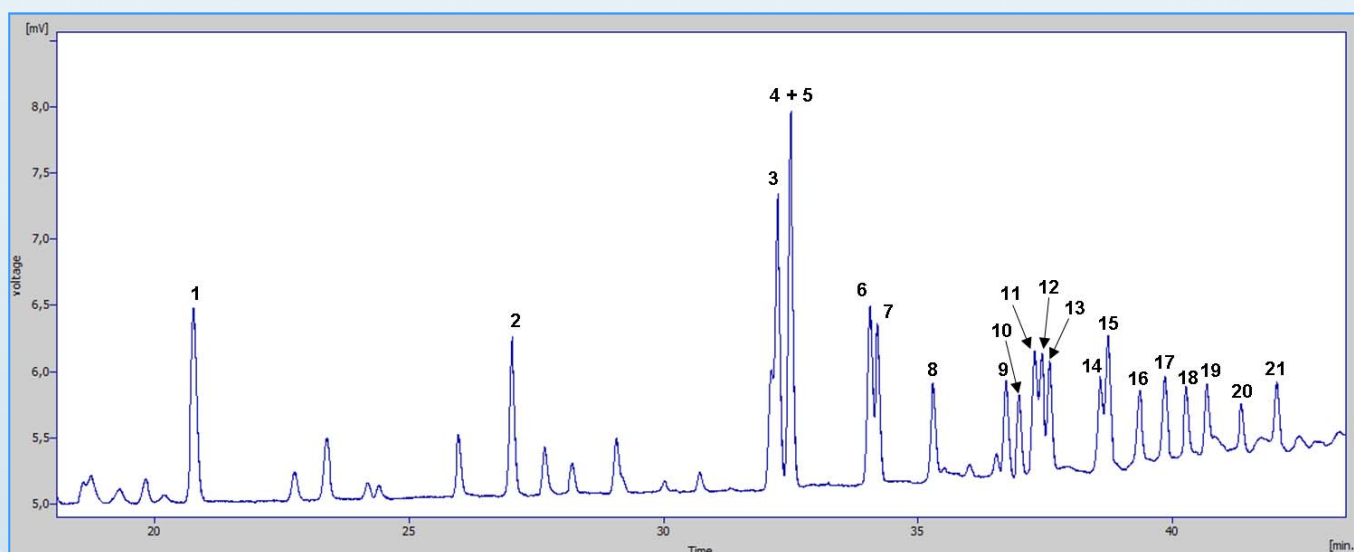


FIGURE 5. DHS-GC-FID chromatogram of the aromatic VOCs mixture (1 ppb). The numbers refer to those in Table 2.

## CONCLUSION

The utilization of the Dynamic Headspace sampler operated in “purging mode” is an advantageous alternative to conventional Purge and Trap systems. MASTER DHS provides overlapped sample thermostating capability, shorter baking phase, and higher sensitivity. In addition, headspace vials are disposable thus eliminating any risk of carry-over effect. No additional workload of cleaning glassware or time-consuming line purging are requested.

The applicability of the proposed method for the determination of aromatic VOCs was confirmed. Thanks to the outstanding concentration efficiency of the dynamic headspace sampling system, low-level detection thresholds required by the latest regulations can be successfully achieved.

## REFERENCES

- [1] DANI Instruments, Application Note - AN 108: *Determination of Volatile Organic Compounds (VOCs) in Water, Part 1: Chlorinated VOCs.*
- [2] *Volatile organic compounds in water by purge and trap capillary column gas chromatography with photoionization and electrolytic conductivity detectors in series.* U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., Method 502.2, revision 2.1, August 1995.