

Determination of Volatile Organic Compounds (VOCs) in Water

Part 1: Chlorinated VOCs

INTRODUCTION

Volatile Organic Compounds (VOCs) are carbon-containing molecules that readily evaporate at normal air temperature. Fuel oils, gasoline, industrial solvents, paints, and dyes are the major sources of VOCs and their improper discharge may cause severe damages to the environment and the human health. Therefore the determination of low concentrations of VOCs is of utmost importance when assessing the quality of drinking and raw source water. The U.S. Environmental Protection Agency (EPA) estimates that VOCs are present in one-fifth of the nation's water supplies. For this reason, government agencies require monitoring of these contaminants at progressively lower levels. Several EPA methods require the use of purge and trap (P&T) systems to extract VOCs from water, although the technique is generally considered to be very burdensome [1].

This study presents the analysis of 37 EPA Method 502.2 targeted chlorinated VOCs by means of Dynamic Headspace-Gas Chromatography (DHS-GC) [2]. The headspace sampling system consists of the MASTER DHS Dynamic Head Space Sampler, equipped with the MASTER AS Automatic Sampler, operated in "purging mode", according to the aforementioned EPA method. The extracted VOCs are then analyzed by GC combined with the highly sensitive and selective Electron Capture Detector (ECD). The obtained results demonstrate that the Dynamic Headspace sampling technique provides a sensitivity exceeding the low-level threshold required by the latest regulations. Data are reported including linear calibrations and method detection limits.

INSTRUMENTATION

In the MASTER DHS, operated in purging mode, the sample is placed in a sealed vial and thermostatted in a temperature-controlled oven. The use of a precise flow of inert gas through an original dual-needle enables the volatiles to be swept from the liquid sample and focused in a sorbent packed trap (see *Figure 1*). The analytes are then rapidly thermally desorbed, passed through the "Dew Stop", to remove most of the water, and introduced directly into the GC system (see *Figure 2*).

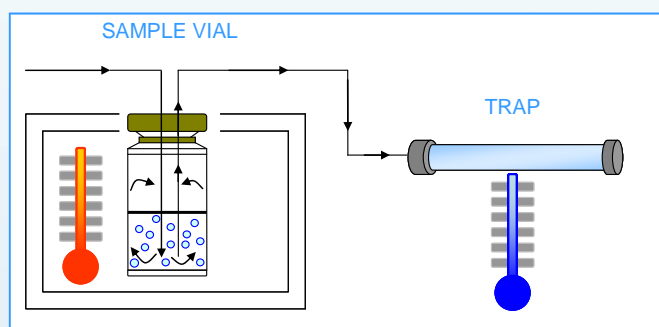


Figure 1. Superior sensitivity is obtained through the constant sweeping of the thermostatted sample, promoting the enrichment of the volatile compounds on the sorbent trap.

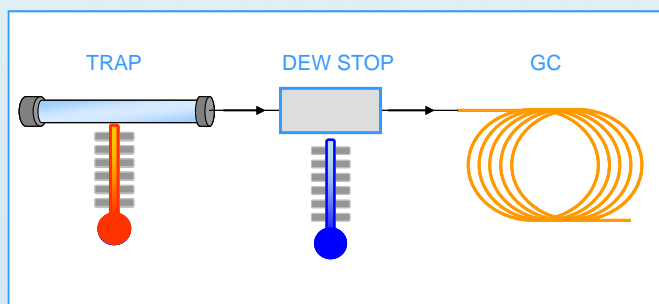


Figure 2. Analytes are rapidly thermally desorbed and passed through the ingenious Dew Stop device which efficiently removes water regardless of the analytes.

In combination with the MASTER AS Automatic Sampler, the MASTER DHS allows sample overlapping with constant incubation time increasing sample capacity and optimizing the vial processing for maximum system productivity.

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-ECD conditions are summarized in *Table 1*.

ECD: The detector is selective to electronegative compounds, e.g. organic compounds containing chlorine and fluorine atoms in their molecules.

It is the first option for environmental measurements, offering excellent performance in the determination of halogenated organic compounds due to the sensitivity 10 to 1,000 higher than the Flame Ionization Detector (FID).

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

TABLE 1. DHS-GC-ECD EXPERIMENTAL CONDITIONS	
MASTER DHS	
Sample Volume	10 mL
Trap Material	Tenax/ Carbotrap/ Carbosieve
Operating Mode	Purging Mode
Valve Temp.	250 °C
Transfer Line Temp.	250 °C
Incubation Temp.	60 °C
Stripping Time	3 min
Stripping Flow	120 mL/min
Trap Stripping Temp.	-10 °C
Injection Time	3 min
Trap Injection Temp.	295 °C
Dew Stop Temp.	0 °C
Baking Time	10 min
Trap Baking Temp.	300 °C
Dew Stop Baking Temp.	200 °C
Baking Flow	80 mL/min
MASTER GC	
Column	Vocol (Supelco) 60 m x 0.32 mm, 3 µm
Oven	35 °C (8 min) at 4 °C/min to 240 °C (1 min)
Injector	SL/IN (220 °C)
Carrier Gas Flow (He)	3.5 mL/min (split 1:2)
Detector	ECD (300 °C, 40 mL/min N ₂)

Calibration

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



Figure 3. The MASTER DHS unit combined with the MASTER AS is easily hyphenated to the MASTER GC.

RESULTS

The chromatogram in *Figure 4* shows the separation obtained for the 1 ppb VOCs mixture. In addition, calibration curves were prepared using a six points curve model, correlation factors (R) are reported in *Table 2*.

Method detectable limits (MDLs) for all the listed target analytes obtained using the same conditions and calculations are listed in *Table 2*. The obtained values were very low and well below currently recommended limits, e.g. EPA Method 502.2. Moreover, excellent precision was attained. MDLs and relative standard deviations (RSD%) cited in the EPA Method 502.2 are also listed for comparison.

High sensitivity is obtained through the constant sweeping of the thermostatted sample, promoting the enrichment of the volatile compounds on the sorbent trap. Moreover, the proper selection of the sorbent materials and trap temperature settings also contribute to the efficient collection and concentration of the target analytes.

The electrical cooling device of the trap and the programmable Dew Stop, which efficiently removes water maintaining volatile compounds recovery unaffected, further enhance sensitivity.

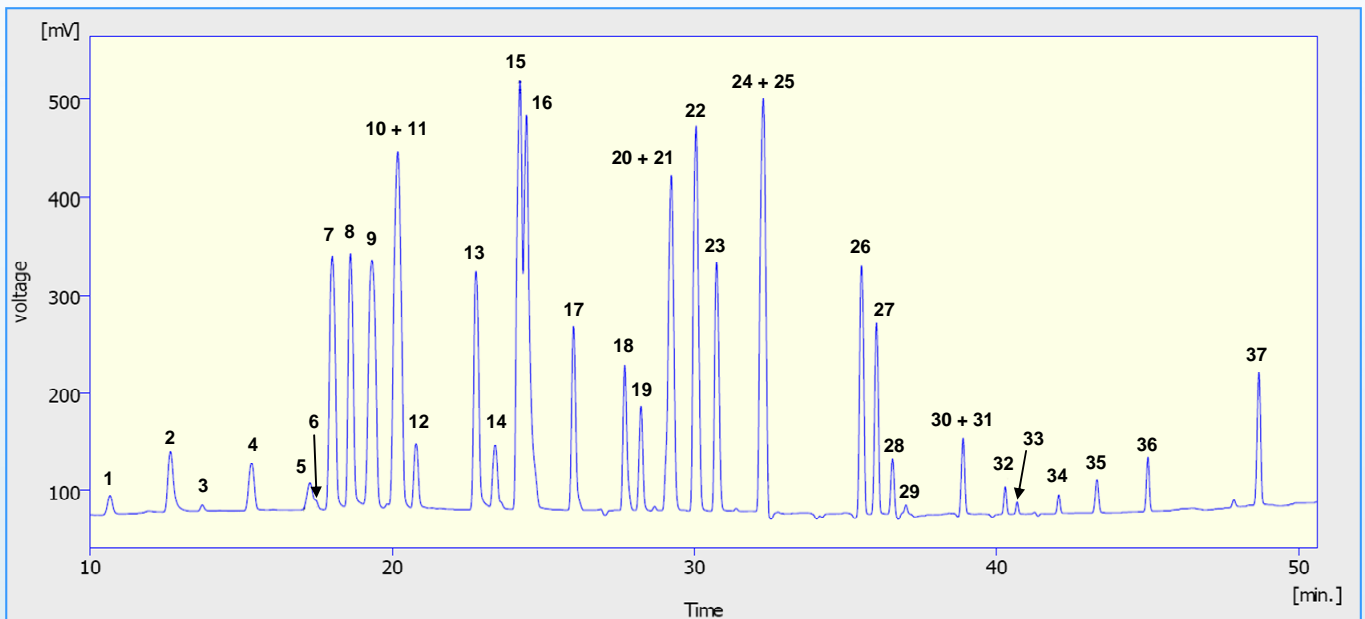


FIGURE 4. DHS-GC-ECD chromatogram of the chlorinated VOCs mixture (1 ppb). The numbers refer to those in Table 2.

TABLE 2. COMPOSITION OF THE CHLORINATED VOCs MIXTURE.

Compounds	Range (ppb)	R	MDL (ppb)	RSD%	EPA 502.2	
					MDL (ppb)	RSD%
1 1,1-Dichloroethylene	0.1 - 2	0.957	0.01	1.5	0.07	2.8
2 Methylene chloride	0.01 - 10	0.996	0.002	2.0	0.02	2.9
3 <i>trans</i> -1,2-Dichloroethylene	0.01 - 10	0.997	0.03	3.0	0.06	3.7
4 1,1-Dichloroethane	0.02 - 2	0.997	0.003	2.2	0.07	5.7
5 2,2-Dichloropropane	0.0002 - 10	0.999	0.005	1.1	0.05	3.4
6 <i>cis</i> -1,2-Dichloroethylene	0.02 - 10	0.999	0.01	16.6	0.01	3.3
7 Chloroform	0.04 - 2	0.985	0.0005	0.8	0.02	2.5
8 Bromochloromethane	0.04 - 1	0.994	0.0005	0.8	0.01	3.0
9 1,1,1-Trichloroethane	0.002 - 2	0.998	0.0005	0.9	0.03	3.3
10 1,1-Dichloropropylene	0.01 - 1	0.994	0.0003	0.7	0.02	3.3
11 Carbon tetrachloride	0.02 - 1	0.997	0.0003	0.7	0.01	3.6
12 1,2-Dichloroethane	0.01 - 1	0.998	0.002	0.5	0.03	3.8
13 Trichloroethylene	0.01 - 1	0.998	0.0005	1.2	0.01	3.6
14 1,2-Dichloropropane	0.002 - 1	0.996	0.002	1.3	0.01	3.7
15 Bromodichloromethane	0.04 - 0.1	0.995	0.0003	0.8	0.02	2.9
16 Dibromomethane	0.01 - 1	0.964	0.0003	1.6	0.02	1.5
17 <i>cis</i> -1,3-Dichloropropylene	0.0002 - 2	0.994	0.0007	2.0	0.06	3.7
18 <i>trans</i> -1,3-Dichloropropylene	0.0002 - 2	0.997	0.001	1.6	0.01	33.7
19 1,1,2-Trichloroethane	0.0002 - 2	0.995	0.0014	1.5	N.D.	5.6
20 1,3-Dichloropropane	0.04 - 2	0.998	0.0004	0.7	0.03	3.1
21 Tetrachloroethylene	0.04 - 2	0.998	0.0004	0.7	0.04	2.5
22 Dibromochloromethane	0.04 - 1	0.960	0.0003	0.5	0.8	2.8
23 1,2-Dibromoethane	0.002 - 1	0.994	0.0005	0.9	2.2	6.7
24 Chlorobenzene	0.01 - 1	0.995	0.0003	0.9	0.01	3.6
25 1,1,1,2-Tetrachloroethane	0.01 - 1	0.995	0.0003	0.9	0.01	2.3
26 Bromoform	0.01 - 1	0.998	0.0005	1.0	1.6	5.2
27 1,1,2,2-Tetrachloroethane	0.0002 - 1	0.999	0.0007	1.6	0.01	6.8
28 1,2,3-Trichloropropane	0.01 - 1	0.997	0.0025	0.8	0.4	2.3
29 Bromobenzene	0.2 - 2	0.995	0.012	1.6	0.03	2.7
30 2-Chlorotoluene	0.02 - 2	0.998	0.002	3.3	0.01	2.7
31 4-Chlorotoluene	0.02 - 2	0.998	0.002	3.3	0.01	3.2
32 1,3-Dichlorobenzene	0.2 - 10	0.999	0.007	0.2	0.02	4.0
33 1,4-Dichlorobenzene	0.4 - 10	0.999	0.018	3.4	0.01	2.3
34 1,2-Dichlorobenzene	0.2 - 10	0.999	0.01	3.0	0.02	1.5
35 1,2-Dibromo-3-chloropropane	0.2 - 2	0.998	0.005	4.0	3.0	11.3
36 1,2,4-Trichlorobenzene	0.1 - 10	0.999	0.004	2.8	0.03	2.1
37 1,2,3-Trichlorobenzene	0.1 - 10	0.999	0.0012	2.5	0.03	3.1

CONCLUSION

The high sensitivity of the system confirmed the applicability of the Dynamic Headspace sampler operated in “purging mode”. The proposed method for the precise and reliable determination of chlorinated VOCs exceeds the low-level threshold required by the latest regulations.

Unlike conventional Purge and Trap systems, the MASTER DHS uses disposable vials thus eliminating any risk of carry-over effects.

In combination with the MASTER AS Automatic Sampler, the MASTER DHS allows sample overlapping with constant incubation time increasing laboratory productivity and sample throughput: the system automatically controls that the next sample is thermostatted during the GC analysis of the previous one.

REFERENCES

- [1] R.L. Grob and E.F. Barry. *Modern Practice of Gas Chromatography*. Wiley, New York, 4th ed., 2004.
- [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.