

# NEXT LEVEL SENSITIVITY AND EFFICIENCY THROUGH COMBINED TECHNOLOGIES

## MONITORING VOLATILE ORGANIC CONTAMINANTS IN WATER AND WASTEWATER USING HEADSPACE GC

### Introduction

Clean water is essential for humans and the environment. Monitoring contaminants in water and wastewater is consequently a big and important field in analytical chemistry. Many substances can be found in water. One group is the volatile organic compound or VOC. They are ubiquitous and include naturally occurring substances, but are also used in industrial and residential products, building materials and paints or cleaners. Part of this group is summed up as so-called BTEX, containing benzene, toluene, ethylbenzene and xylene. They can be found in mineral oil and its products and are utilized as raw materials in the chemical industry. Many VOCs and all BTEX are toxic and harmful to humans and the environment; some of them can cause cancer. Monitoring of these substances with detection limits down to trace level concentrations is therefore essential, typically performed using the gas chromatography (GC) technique.

### Analytical setup choice

In chemical analyses, sample preparation is one of the most time-consuming steps. When analyzing water, direct injection of the water sample into the GC is usually not possible or at least not preferred. Additionally, sample pre-concentration steps may be needed to reach detection limits required by regulations. In the case of VOCs and BTEX in water, headspace injection into the GC is the method of choice. Due to the integrated headspace oven, the target substances migrate to the gas phase during incubation time, and a prescribed amount of this gas phase is transferred into the GC, either via gas tight syringes or transfer line setups with or without loop. This way, the water samples can be analyzed directly, skipping lengthy sample preparations needed by liquid-liquid or solid phase extraction [1].

In this study, the analysis was performed by a GC-2030 system equipped with HS-20 headspace sampler (both Shimadzu). HS-20 was chosen due to its short transfer-line which reduces the risk of carryover and loss of analytes. Additionally, it offers the possibility to overlap multiple incubations for consecutive samples, helping to minimize analytical run times.

Detector choice needs to be based on the sensitivity for the respective target substances to achieve regulatory levels. Flame ionization detectors (FID) are general detectors for all kinds of hydrocarbons, and cover a broad range of analytes. Sensitivity may not however be high enough to reach regulatory levels for all target compounds. For such cases, selective detectors covering certain target substances may be beneficial. Electron capture detection (ECD) is the detector of choice for VOCs due to its increased sensitivity to electrophilic compounds such as halogenated substances. For highest flexibility in the work presented here, both FID and ECD detection were chosen to be investigated.

### Experimental

#### Target compounds

For both target groups, standard solutions are commercially available. The target compounds of VOCs were vinyl chloride, 1,1-dichloroethene, chloroform, 1,1,1-trichloroethane, tetrachloromethane, benzene, 1,2-dichloroethane, trichloroethene, bromodichloromethane, dibromochloromethane, bromoform and 1,4-dichlorobenzene. The standard solution for BTEX contained benzene, toluene and ethylbenzene as well as para-, ortho- and meta-xylene.

#### Method optimization

To optimize sensitivity in headspace analysis, the amount of substance in the gas phase after incubation needs to be maximized. This is a factor of different parameters, e.g. the ideal incubation time and the sample filling volume, as the latter determines the phase ratio between gas and liquid phase in the vial. Different target substances may need different parameter values due to compound dependent distribution-coefficients [1].

To determine the optimum vial filling volume, a 10 µg/L standard was measured in a 20 mL vial with increasing volumes from 5 to 15 mL. The plot of the area of ethylbenzene against volume is shown in figure 1. A significant upward trend of the area could be observed until 15 mL volume; the graphs of the other compounds showed a similar trend. Consequently, a vial filling volume of 15 mL was used.

Optimum equilibration time was found by measuring a solution of 1 µg/L with increasing equilibration times between 3 and 24

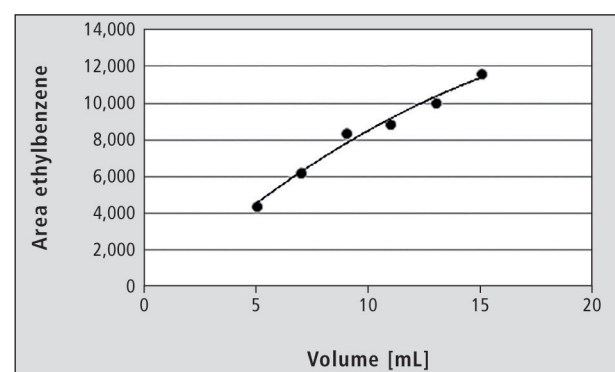


Figure 1: Area of ethylbenzene peak as a factor of vial volume

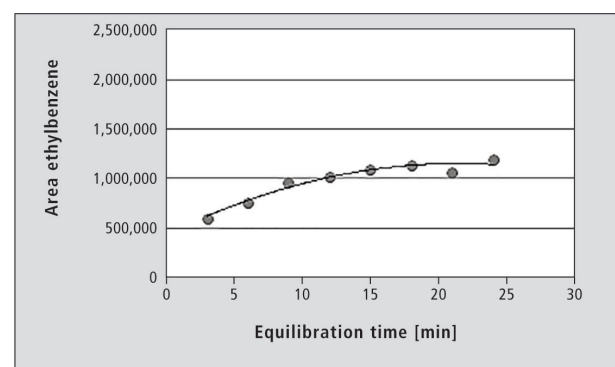


Figure 2: Area of ethylbenzene peak as a factor of equilibration time

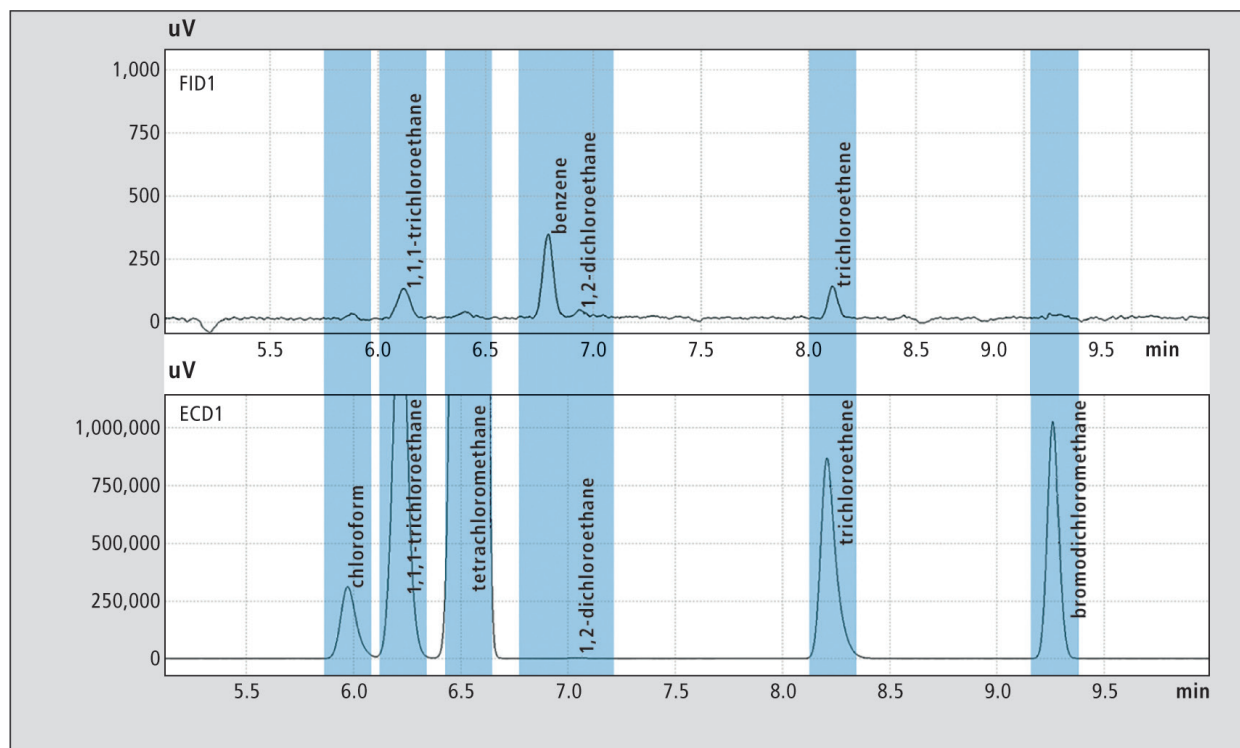


Figure 3: Comparison of chromatogram excerpts of VOC standard mixture at 1 µg/L on FID (top) and ECD (bottom)

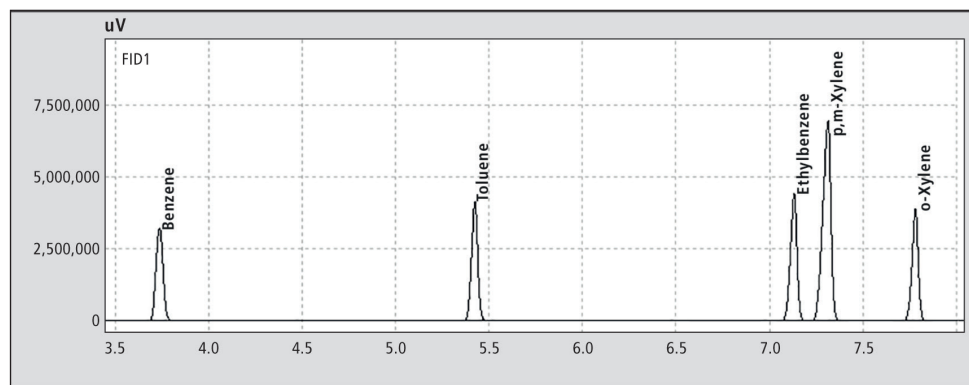


Figure 4: Chromatogram of BTEX standard mixture at 10 mg/L

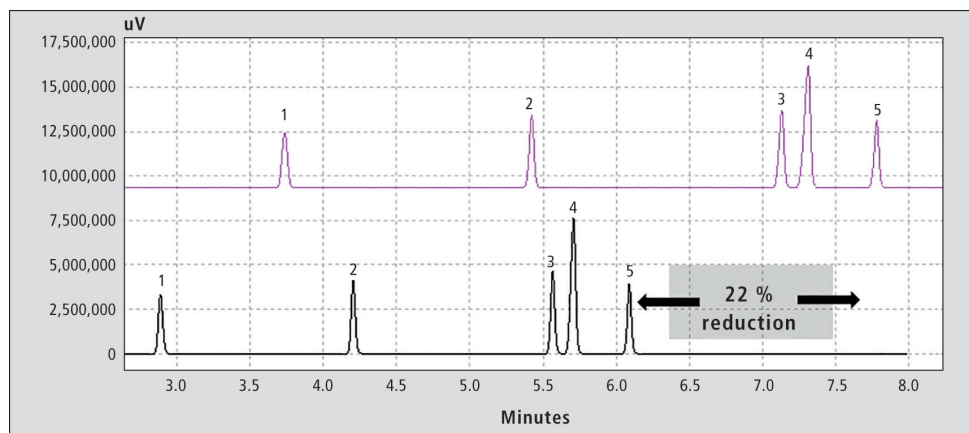


Figure 5: Comparison of the chromatograms of standard mixture at 10 mg/L with helium and hydrogen as carrier gas

minutes. A plot of peak area of ethylbenzene against equilibration time is shown in figure 2. A significant upward trend of the area can be noticed until around 15 min, and similar graphs were obtained for all other compounds. Consequently, 15 min were chosen as final equilibration time for BTEX. For VOCs, slightly longer incubation times have shown to be beneficial, which is why incubation for these substances was set to 20 min.

**Experimental conditions**

For the analysis of VOCs and BTEX, headspace vials were filled with 15 mL distilled water and the standard solution was added at the respective concentration. For BTEX, the dilution series had concentrations between 100 ng/L and 10 mg/L. For VOCs detected by FID, solutions with concentrations between 500 ng/L and 100 µg/L were prepared. Because of the higher sensitivity of ECD, VOCs were measured in a concentration range of 0.5 ng/L to 10 µg/L. To minimize loss of these highly volatile substances, piston pipettes or syringes were used to prepare the dilution series.

The solutions were incubated for 15 min (BTEX) and 20 min (VOCs) at 70 °C in the headspace sampler before injection to the GC. Chromatographic separation was done using a SH-Rxi-624Sil MS column (Shimadzu) with a length of 30 m, 0.25 mm inner diameter and 1.4 µm film thickness. Total chromatographic runtime for VOCs was 15 minutes and 8 minutes for BTEX. In both cases helium was used as carrier gas.

**Results**

**VOCs**

Figure 3 shows part of a chromatogram taken from VOCs at 1 µg/L with FID (top) and ECD (bottom) detection. Whereas benzene, 1,1,1-trichloroethane and trichloroethene are clearly visible at this concentration in the FID chromatogram, the signal intensity for chloroform, tetrachloromethane and bromodichloromethane is much lower. In contrast, with ECD detection the corresponding signals for the latter three compounds are much more pronounced. A correlation between sensitivity increase and number of halogen atoms in the compound becomes evident when comparing the response of the dichlorinated, trichlorinated and tetrachlorinated substances. With the chosen detectors,

it is possible to monitor VOCs down to trace level concentrations. The concentrations summarized in table 1 are the lowest levels measured for the respective compounds with the target peak showing a response with a signal-to-noise ratio (S/N) greater than 3. Based on universal detection capabilities of the FID, all 12 compounds can be detected, whereas the ECD is only capable of detection of 10 compounds, while giving no response for benzene and vinyl chloride. The remaining 10 compounds show higher responses compared to FID, leading to lower limits of detection for these substances on ECD. The lowest concentrations measured with ECD were up to a thousand times lower than concentrations measured with the FID (see table 1).

Are these low levels really needed? Official regulations such as the European drinking water directive Council Directive 98/83/EC set the limits for target compounds that may affect the quality of water intended for human consumption. This directive sets the maximum allowed levels of benzene and 1,2-dichloroethane at 1.0 µg/L and 3.0 µg/L respectively [2]. In the case of benzene, the limit is easily met with FID detection. For 1,2-dichloroethane, in contrast, the detection limit of the FID is not sufficient to fulfill the requirements of the directive. Using ECD detection, the lowest level measured is 10 times lower, easily meeting the directive.

Additionally, calibration for the VOCs was performed from the lowest level with S/N higher than 3 upwards, leading to a linear regression R<sup>2</sup> of greater or equal to 0.999, with the exception of 1,1-dichloroethene for ECD and dibromochloromethane and 1,4-dichlorobenzene for FID showing R<sup>2</sup> of 0.998.

**BTEX**

The chromatogram of the BTEX standard solution is shown in figure 4. It consists of five well separated peaks. The isomers p- and m-xylene are eluting together, o-xylene is eluting separately as the last compound.

For all BTEX compounds, the lowest concentration measured showing a response with S/N higher than 3 was 1 µg/L. The signal-to-noise ratios obtained at this level as well as the corresponding retention times are shown in table 2. Based on the lowest level of 1 µg/L, a 5-level calibration curve was created for all BTEX compounds. All resulting curves showed an R<sup>2</sup> of 0.9998.

**Time-saving potential with hydrogen as carrier gas**

Helium is still the most common carrier gas for GC analysis. But limited availability and increasing prices make users search for alternatives. Hydrogen is a valuable alternative as it is lower in cost than helium and, as a gas with a flat Van Deemter curve, provides great separation in a wide linear velocity range [3]. This enables shorter analysis times when using hydrogen as carrier gas. In this work the time-saving potential was investigated on the example of the already short analysis of BTEX. When using helium, the linear velocity of the carrier gas was chosen to be 45 cm/s, whereas with hydrogen the value was increased to 60 cm/s, combined with an adjusted oven temperature program.

This led to a shorter analysis time as shown in figure 5 comparing the chromatograms of the standard mixture at 10 µg/L measured with helium (pink) and hydrogen (black). o-Xylene is eluting

Compound	Retention time [min]	FID		ECD	
		LLC* [µg/L]	S/N	LLC* [µg/L]	S/N
vinyl chloride	1.55	0.50	3.13	—	—
1,1-dichloroethene	2.65	0.50	3.12	0.001	8.29
chloroform	5.86	5.00	4.79	0.0005	37.96
1,1,1-trichloroethane	6.12	1.00	4.96	0.0005	11.27
tetrachloromethane	6.40	5.00	5.87	0.0005	39.46
benzene	6.79	0.50	6.10	—	—
1,2-dichloroethane	6.94	5.00	6.45	0.50	9.22
trichloroethene	8.11	1.00	5.34	0.0005	9.02
bromodichloromethane	9.17	5.00	3.15	0.001	5.39
dibromochloromethane	11.64	10.00	6.07	0.001	3.71
bromoform	13.06	10.00	3.63	0.005	16.83
1,4-dichlorobenzene	14.30	0.50	5.27	0.05	10.58

Table 1: Retention times, S/N and \*LLC (concentration of the lowest level measured showing compound response above S/N=3) of VOCs on FID and ECD

Compound	Retention time [min]	LLC* [µg/L]	S/N
benzene	3.74	1.00	9.92
toluene	5.42	1.00	14.04
ethylbenzene	7.13	1.00	15.43
p-,m-xylene	7.32	1.00	25.09
o-xylene	7.78	1.00	12.67

Table 2: Retention times, S/N and \*LLC (concentration of the lowest level measured showing compound response above S/N=3) of BTEX

as the last compound at a retention time of 7.8 minutes with helium as carrier gas. Using hydrogen, it elutes more than 1.5 minutes earlier at 6.1 minutes, leading to an analysis time shortened by 22 %. The shorter analysis time did not compromise separation efficiency, as seen when comparing the resolution between peak 3 and 4 which is 2.6 with helium and 2.5 with hydrogen. Comparison of the detection limits of measurements with helium shows that no loss of sensitivity could be observed.

## Conclusion

The combination of FID and ECD detection makes it possible to meet the detection limits given by regulations for volatile target substances in water and wastewater analysis. Whereas FID detects all VOC and BTEX target compounds, ECD only sees the halogenated substances but provides very low detection limits down to 0.0005 µg/L for several components. GC systems with

headspace sampling allow sensitive analysis of water samples without the need for time-consuming sample preparation. Additional time saving can be realized using hydrogen as carrier gas, reducing chromatographic runtime even for the already short analysis of BTEX by more than 20%.

## References

- [1] A Technical Guide for Static Headspace Analysis Using GC, Restek, 2000
- [2] European Council Directive 98/83/EC
- [3] H.-J. Hübschmann, Handbook of GC-MS, Wiley-VCH, 2015

## Biographies

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