Application Note 10452

Analysis of BTEX and Chlorinated Compounds in Water Via a Dual Detector Configuration Gas Chromatograph

Andrea Caruso
Thermo Fisher Scientific, Milan, Italy

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Chromeleon Chromatography Data System Software, Environmental, Gas Chromatography, Headspace, Headspace Autosampler, TRACE 1310 Gas Chromatograph, TriPlus 300, Water Pollutants, Water Quality

Goal
To describe the determination of benzene, toluene, ethylbenzene, and xylenes, along with several chlorinated volatile compounds in water using a Thermo Scientific™ TriPlus™ 300 Headspace autosampler, Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC), and Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software.

Introduction
Chemical pollutants from various sources are a constant threat to the hydrosphere. Considering the impact that water pollution exerts on the surrounding environment, it is crucial to monitor and prevent any possible source of water contamination. Examples of water pollutants include volatile compounds such as benzene, toluene, ethylbenzene, xylenes, and chlorinated hydrocarbons. Their high volatility makes it possible to remove these pollutants from water samples using a static headspace technique. The unique chemical nature of these compounds makes them ideal targets of analysis for different detectors. Where the hydrocarbons are easily detected and quantitated using a flame ionization detector (FID), the chlorinated compounds require a more selective detector such as an electron capture detector (ECD).

A double detector configuration enables simultaneous analysis of both classes of compounds: the effluent from the column is split and sent to the two detectors via a dual detector kit, which guarantees inertness of the sample path and no dead volumes or cold spots. The analysis can be performed using the TRACE 1310 gas chromatograph equipped with these dual detectors and a TriPlus 300 Headspace autosampler, controlled by the Chromeleon CDS software. This system enables reproducible and reliable automated sample analysis and data processing.

Experimental
This analysis used a TriPlus 300 Headspace autosampler and a TRACE 1310 GC. The data were collected and processed using Chromeleon 7.2 CDS software. The system was equipped with one Instant Connect Split/Splitless (SSL) injector with a dedicated headspace liner (P/N 453A1335). An Instant Connect FID and an Instant Connect ECD were mounted on the GC. A dual detector microfluidic kit (P/N 19071030) was mounted in the oven and guaranteed a 50% split of the column flow to each detector.

Restek DW-VOC Mix #2 (P/N 30220) was used as the standard for calibration in addition to individual standard solutions of benzene, chloroform, carbon tetrachloride, and 1,2,4 trichlorobenzene. The calibration points were prepared using successive dilutions from a stock solution at 200 ppm in water:methanol, 10:1.

Eight calibration levels were prepared for the analytes at 1, 10, 50, 100, 500 ppb, and 1, 5 and 10 ppm. The chlorinated compounds were calibrated from 1 to 100 ppb while the FID-responsive compounds were calibrated from 50 ppb to 10 ppm.

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Analysis

The sample for analysis was 5 mL of water in a 20 mL vial (La-Pha-Pack P/N 18091307). The vial was tightly closed with a magnetic screw cap (La-Pha-Pack P/N 18031414).

Analytical Conditions

TriPlus 300 Headspace Autosampler	
Equilibration Time:	20 min, shaking at high
Oven Temperature:	85 °C
Manifold Temperature:	95 °C
Transfer Line Temperature:	95 °C
Pressurization Mode:	Pressure, 1 bar, equilibration time 0.2 min
Loop Filling Mode:	Pressure, 0.5 bar, equilibration time 0.2 min
Loop Size:	1 mL
Injection Mode:	Standard, injection time, 0.5 min
Purge:	After 1 min at 100 mL/min, in addition to standard purging time
Vial Venting:	On

TRACE 1310 GC	
Liner:	Dedicated headspace liner (P/N 453A1335)
Carrier Gas:	Helium, constant flow, 3 mL/min
Column Type:	TG-624 30 m, 0.32 mm, 1.8 µm (P/N 26085-3390)
Column Oven:	Initial 50 °C, hold 1.0 min. Ramp at 10 °C/min up to 190 °C. Hold 1 min

Instant Connect SSL Injector	
Inlet Temperature:	200 °C
Mode:	Split mode, flow 45 mL/min, split ratio 15:1

Instant Connect FID	
Temperature:	250 °C

Instant Connect ECD	
Temperature:	250 °C
Makeup Gas:	Nitrogen, 15 mL/min
Reference Current:	0.5 nA
Pulse Amplitude:	50 V
Pulse Width:	1 µs

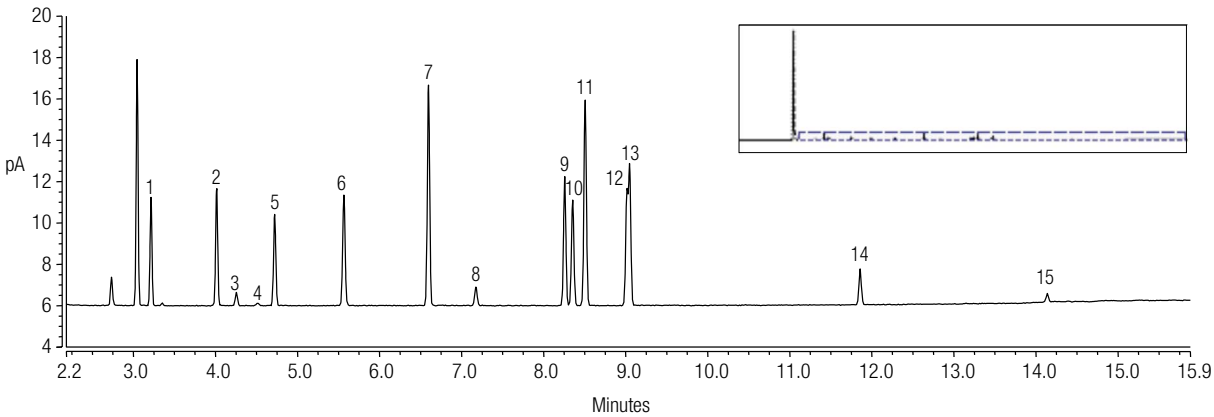
Results and Discussion

Results of the FID calibration can be found in Table 1. A six-point calibration curve was prepared at concentrations of 50, 100, 500, 1000, 5000, 10,000 ppb for each compound. All the analytes show very good correlation coefficients.

Table 1. FID calibration linearity results.

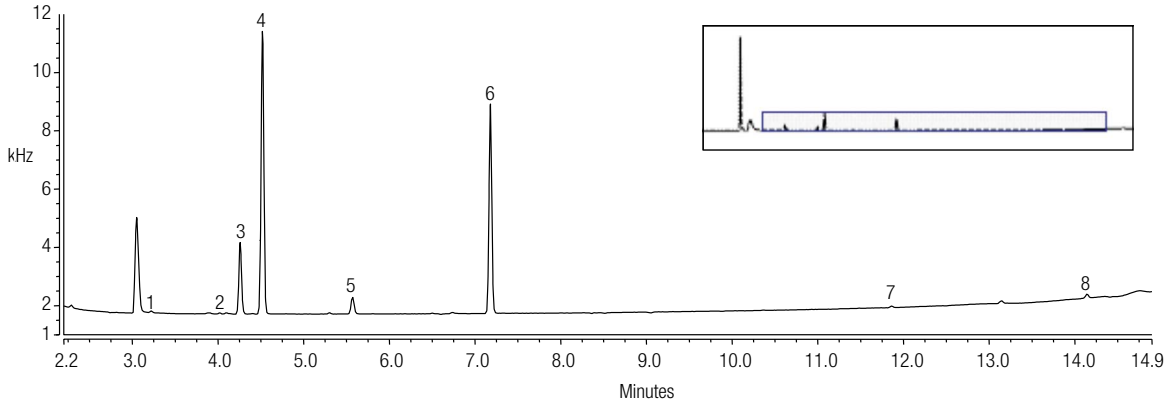
Analyte	Coeff. of Determination
benzene	0.998
toluene	0.998
chlorobenzene	0.999
ethylbenzene	0.998
m/p xylene	0.999
o xylene	0.997
styrene	0.998

Figure 1 shows the FID chromatogram acquired at a 1 ppm concentration.



Peaks:
1. cis-1,2-Dichloroethene
2. trans-1, 2-Dichloroethene
3. Chloroform
4. Benzene
5. Carbon tetrachloride
6. Dichloropropane
7. Toluene
8. Tetrachlorethene
9. Chlorobenzene
10. Ethylbenzene
11. m/p Xylene
12. o Xylene
13. Styrene
14. 1,2-Dichlorobenzene
15. 1,2,4-Trichlorobenzene

Figure 1. FID chromatogram at 1 ppm.



Peaks:
1. cis-1,2-Dichloroethene
2. trans-1, 2-Dichloroethene
3. Chloroform
4. Carbon tetrachloride
5. Dichloropropane
6. Tetrachloroethene
7. 1,2-Dichlorobenzene
8. 1,2,4-Trichlorobenzene

Figure 2. ECD chromatogram at 10 ppb.

The FID detector was capable of detecting all of the compounds. The ECD, however, is suitable for detecting only chlorinated compounds, but achieves far better sensitivity with this class of volatiles.

The calibration results and the chromatogram acquired at 10 ppb for the ECD are reported in Table 2 and Figure 2, respectively.

A five-point calibration curve was prepared for the ECD-responsive analytes at 100, 50, 10, 5, 1 ppb.

Area repeatability for the detected species was tested at 500 ppb on the FID. The measured RSD was always 1–3%.

Deionized water samples were analyzed after each sequence of 10 samples to exclude the possibility of carryover and to provide a clear baseline.

Table 2. ECD calibration linearity results.

Analyte	Coeff. of Determination
cis 1,2 dichloroethene	0.991
trans 1,2 dichloroethene	0.999
chloroform	0.997
carbon tetrachloride	0.999
dichloropropane	0.992
tetrachloroethene	0.991
1,2 dichlorobenzene	0.999
1,2,4 trichlorobenzene	0.999

Table 3. ECD area repeatability results.

Compound	RSD%
cis-1,2-Dichloroethene	1.69
trans-1,2-Dichloroethene	1.62
Chloroform	2.70
Benzene	1.69
Dichloropropane	1.32
Toluene	1.59
Chlorobenzene	1.63
Ethylbenzene	1.08
m/p Xylene	1.45
o Xylene	2.44
Styrene	1.47
1,2-Dichlorobenzene	2.02
1,2,4-Trichlorobenzene	2.20

Conclusions

The results confirm that a system comprised of a TriPlus 300 Headspace autosampler, a TRACE 1310 GC, and Chromeleon CDS software is a reliable and automated solution for the detection and screening of aromatic and chlorinated compounds in water.

The system guarantees excellent throughput with its 120-vial sample tray and the large, 18-vial incubation oven overlap capacity. The inertness of the entire sample path and high temperature capability eliminate any carryover effect, ensuring the highest sample integrity and consistency in results. The optional barcode capabilities of the autosampler and the accurate auditing capabilities of the Chromeleon CDS software ensure the highest data quality and traceability for use in regulated environments.

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