

Analysis of Volatile Halogenated and Aromatic Hydrocarbons and Organophosphorus Pesticides in Water with a Versatile Agilent 7890B Gas Chromatography System and an Agilent 7697A Headspace Sampler

Application Note

Environmental

Authors

Chunxiao Wang
Agilent Technologies (Shanghai) Co Ltd.
412 YingLun Road
Waigaoqiao Free Trade Zone
Shanghai 200131
P.R. China

Jingqiang Zhang, and ShunNa
Agilent Technologies (China) Co Ltd.
5F, 18F Citic Plaza ShenHong Square
No. 1350 North Sichuan Road
Hongkou District, Shanghai 200080
P.R. China

Abstract

An Agilent 7890B GC system configured with three detectors: (1) ECD (Electron capture detector), (2) FID (Flame ionization detector), and (3) FPD (Flame Photometric Detector) was used for the analysis of volatile halogenated and aromatic hydrocarbons and organophosphorus pesticides in water. The headspace sampler (HS) vial temperature and time for sample equilibration were optimized, allowing simultaneous analysis of aromatic and halogenated hydrocarbons with FID and ECD in one HS injection. The FPD channel with automated liquid sampler (ALS) was used for organophosphorus pesticides analysis. The repeatability was generally better than 2.0% RSD for each aromatic and halogenated hydrocarbons. The repeatability and recovery range for organophosphorus pesticides are 1.45–2.74% and 90.4–98.8%, respectively.



Agilent Technologies

Introduction

Volatile halogenated and aromatic hydrocarbons as well as organophosphorus pesticides have a variety of harmful health effects. The U.S. Environmental Protection Agency (EPA) estimates that volatile organic compounds are present in one-fifth of the nation's water supplies. They can enter ground water from a variety of sources. Benzene, for example, may enter ground water from gasoline or oil spills on the ground surface or from leaking underground fuel tanks.

Usually, a large number of samples need to be processed routinely, and therefore, a high degree of automation is required with minimal sample prep for cost reduction. Static HS/GC is well suited and widely used for volatile halogenated and aromatic hydrocarbon determinations. The FPD performs well for trace organophosphorus pesticide analysis. Therefore, a 7890B GC system with three channels (ECD, FID, and FPD) forms a versatile system suited for routine analysis of volatile aromatic and halogenated hydrocarbons and organophosphorus pesticides in water.

Experimental

Figure 1 shows a 7890B GC system configured with FID, ECD, and FPD.

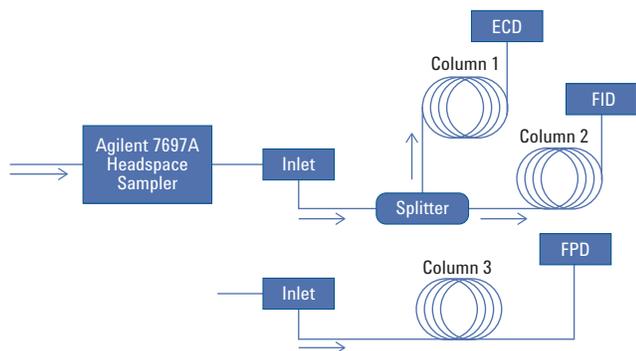


Figure 1. Agilent 7890B GC three channel configuration.
 (1) FID channel with HS: for aromatic hydrocarbons
 (2) ECD channel with HS: for halogenated hydrocarbons
 (3) FPD channel with ALS: for organophosphorus pesticides

Table 1. Typical GC Conditions

Volatile aromatic and halogenated organic compounds method

Agilent 7890B GC

Inlet	Split/Splitless	
	Temperature:	150 °C
Column	Split vent:	50 mL/min
	Column 1:	19091s-413UI, HP-5 MS UI, 30 m × 0.32 mm, 1 µm
	Column 2:	123-3234, DB FFAP, 30 m × 0.32 mm, 1 µm
Carrier gas	N ₂ at 2.5 mL/min constant flow	
Oven temperature	40 °C (2 minutes) to 120 °C at 6 °C/min	
Detector	ECD: Temperature:	320 °C,
	Makeup:	N ₂ at 30 mL/min
	FID: Temperature:	200 °C,
	H ₂ /Air:	40 mL/min/400 mL/min

Agilent 7890B GC7697A Headspace Sampler

	20-mL vials	
Temperature	HS oven:	70 °C
	Valve/loop:	70 °C
	Transfer line:	100 °C
Time	Vial equilibration time:	40 minutes
	Inject time:	0.5 minutes
Vial sampling parameters	Vial pressurize value:	15 psi
	Vial final sampling pressure:	10 psi
	Loop size:	1 mL

Organic phosphorus method

Inlet	Split/Splitless	
	Temperature:	230 °C
	Splitless mode, 30 mL/purge flow at 0.75 minutes	
Sample size	1 µL	
Column	DB-1701, 30 m × 0.25 mm, 1 µm	
Carrier gas	N ₂ at 1 mL/min constant flow	
Oven temperature	100 °C to 170 °C at 25 °C/min to 210 °C (1 minute) at 15 °C/min to 220 °C at 10 °C/min to 240 °C (5 minutes) at 15 °C/min	
Detector	FPD Plus	
	Temperature:	270 °C
	Emission block:	150 °C

Results and Discussion

Volatile aromatic and halogenated hydrocarbons analysis

A dual-channel ECD and FID was used for simultaneous static headspace analysis of volatile aromatic and halogenated hydrocarbon in water. Figure 1 shows the configuration.

A deactivated retention gap connected the inlet to an unpurged splitter yielding a 1 to 1 split into 30 m × 0.32 mm HP-5 and DB-FFAP columns. Aromatic and halogenated compounds were separated and detected by DB-FFAP (Column 2) with FID and HP-5 MS UI (Column 1) with ECD, respectively.

Headspace parameter optimization

The influence of temperature and sample equilibration time on headspace sensitivity was investigated.

An increase in temperature decreases the value of the partition coefficient, k . The actual influence on headspace sensitivity of this change depends on the relative value of k versus the phase ratio β . If k is much greater than β , headspace sensitivity depends directly on k : the higher the temperature, the

higher the headspace sensitivity. However, if k is smaller than β , then the headspace sensitivity is determined by the value of the phase ratio β . In this case, the thermostating temperature has almost no influence on headspace sensitivity [1]. The concentration in the gas phase can be expressed according to the following equation: $C_g = C_o / (k + \beta)$, where C_g is the concentration of analyte in the gas phase and C_o is the original concentration of the analyte in the matrix.

To investigate the temperature effect, five vials with the spiked water sample containing all target aromatic and halogenated compounds with the same concentration of each compound were prepared. Thermostating them was performed with increasing temperatures, with other temperatures remaining constant. The sample volume was 9 mL in a 20-mL vial. Figure 2 shows the plot of the obtained peak area against the increasing sample temperature. The influence of temperature in principle is an analyte-specific function. In this application note, it is observed that the increase in temperature enhances the headspace sensitivity for target compounds, but at different levels. The peak areas for most compounds reached the maximum when the sample temperature was 70 °C.

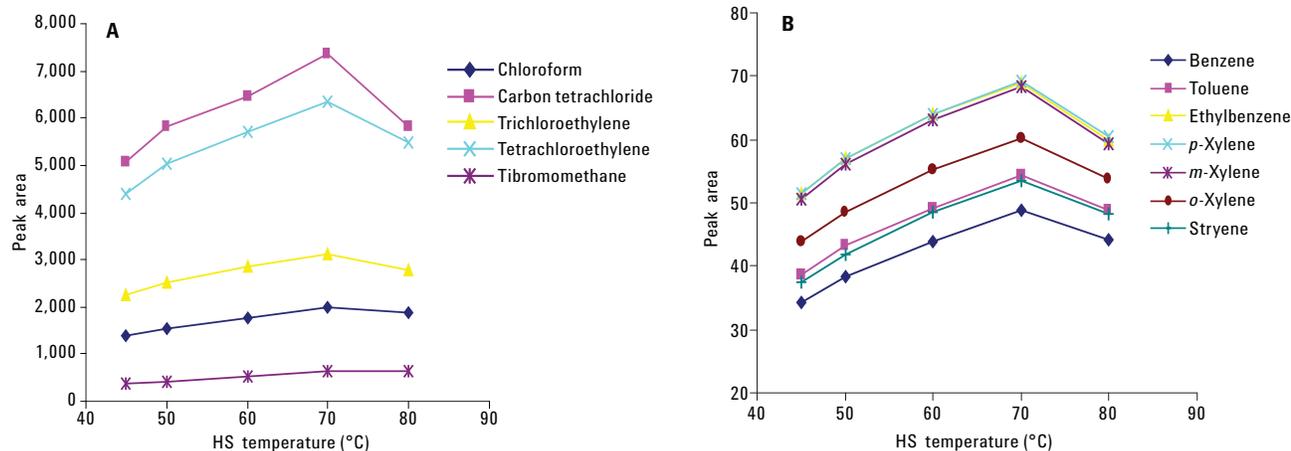


Figure 2. HS temperature versus peak area for halogenated A) and aromatic hydrocarbons B) in water.

Equilibration time

To investigate the optimal equilibration time, six vials with the spiked water sample containing all target aromatic and halogenated compounds with the same concentration of each compound were equilibrated for different times but otherwise using identical conditions. The obtained peak area was then plotted against the thermostating time. As shown in Figure 3, the peak does not increase when the thermostating time was over 40 minutes. According to Figures 2 and 3, 70 °C and 40 minutes were selected as the sample equilibration temperature and time.

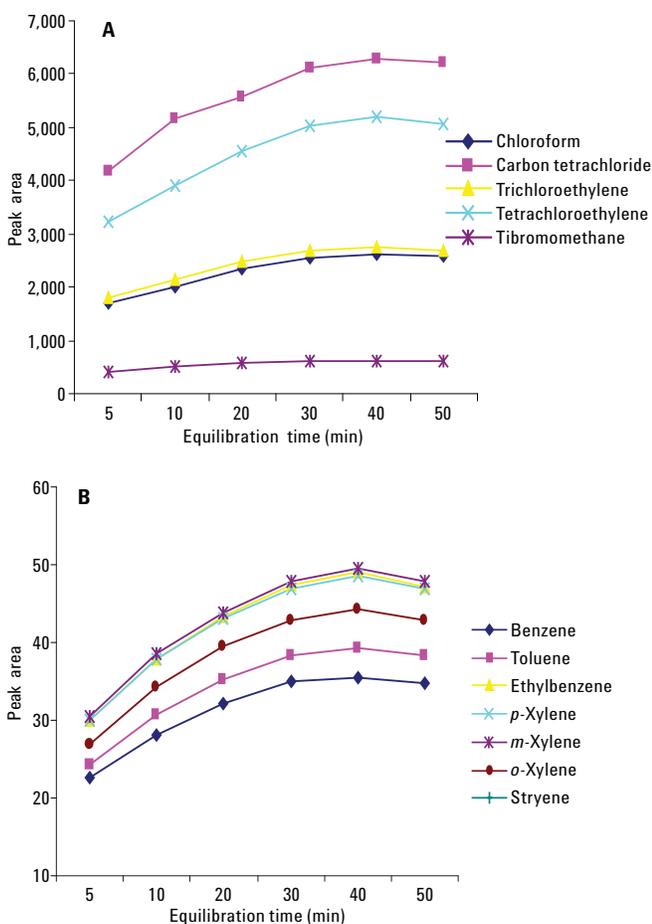


Figure 3. Equilibration time versus peak area for halogenated **A** and aromatic hydrocarbons **B** in water.

Sample loop temperature

The thermal zone design of the Agilent 7697A headspace sampler removes the need to operate the oven loop and headspace oven zones at different temperatures [2]. The best peak area reproducibility from the 7697 headspace sampler is observed when the oven and loop zones are operated at the same temperature. In the 7697A design, the vial is thermally equilibrated in the HS oven for a requisite amount of time then the vial is physically moved the loop zone for sampling. A thermodynamic equilibrium is established within the vial while the vial is in the HS oven; to maintain that equilibrium the vial's temperature must remain constant. When the loop zone of the 7697A HS oven is set to the same temperature as the oven then the vial's equilibrium is maintained.

Repeatability and recovery

Spiked water samples were analyzed for this study. The resulting data is shown in Table 2. The relative standard deviation (RSD) is better than 2.0% and recovery ranges between 97.3 and 102.7%. Figure 4 shows the chromatogram.

Table 2. Repeatability and Recovery for Volatile Halogenated and Aromatic Hydrocarbons

Compound name	RSD % (n = 7, excluded 1st run)				Recovery (%)
	Average Concentration (µg/L)	RSD%	Average Retention time (min)	RSD%	
Chloroform	3.98	1.82	2.15	0.016	99.59
Carbon tetrachloride	1.95	1.74	2.49	0.017	97.33
Trichloroethylene	3.98	1.51	2.86	0.013	99.44
Tetrachloroethylene	1.98	1.33	4.61	0.007	99.00
Bromoform	4.05	1.92	6.25	0.006	101.23
Benzene	406.86	1.94	5.30	0.009	101.71
Toluene	407.15	1.85	7.48	0.006	101.79
Ethylbenzene	406.65	1.60	9.54	0.012	101.66
p-Xylene	406.54	1.55	9.75	0.006	101.63
m-Xylene	406.39	1.58	9.92	0.006	101.60
o-Xylene	406.73	1.68	11.04	0.006	101.68
Styrene	410.80	1.87	12.84	0.005	102.70

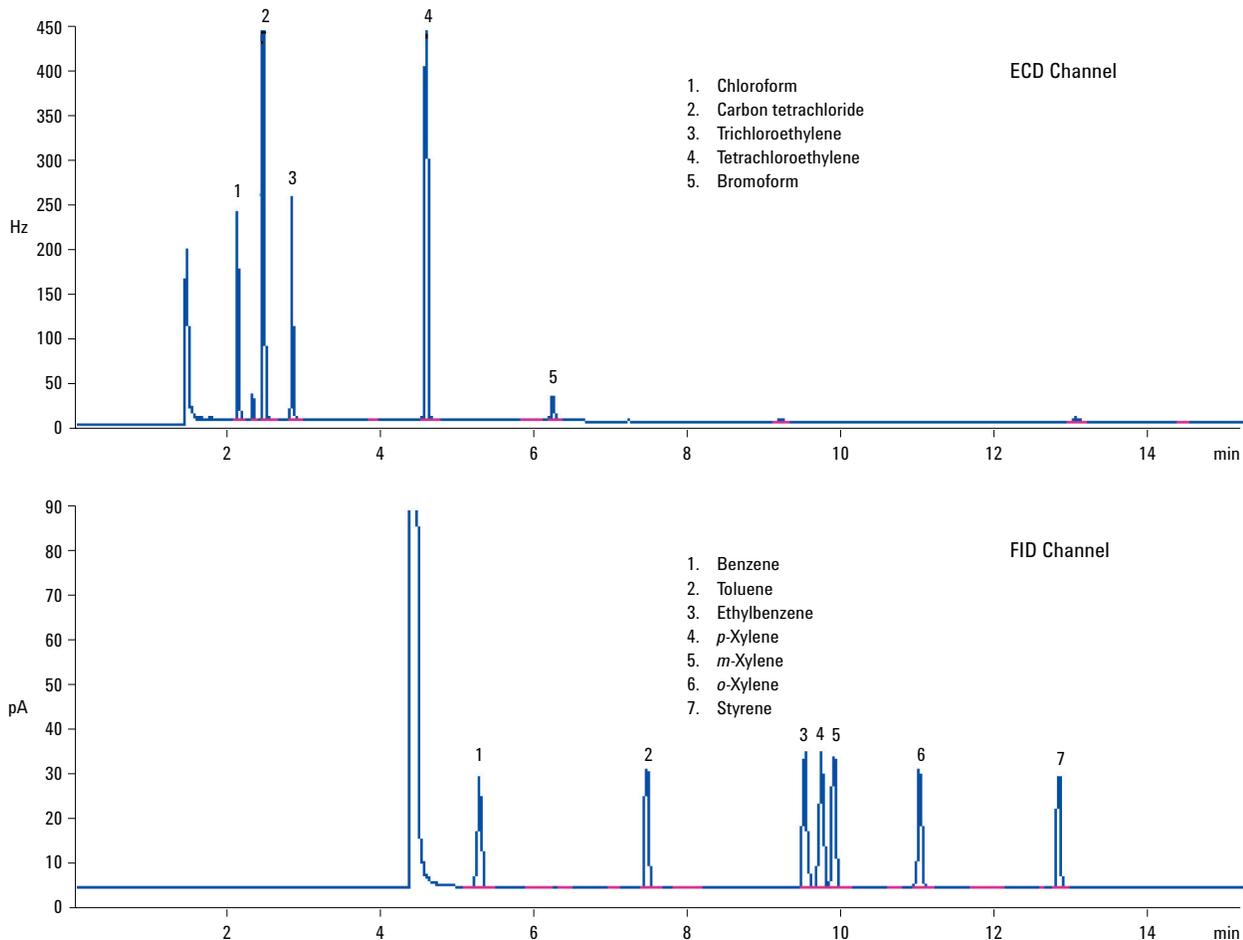


Figure 4. Simultaneous analysis of volatile halogenated and aromatic hydrocarbons in water.

Organophosphorus pesticide analysis

Organophosphorus pesticides were separated with a DB-1701 column and ALS injection. The FPD was used for detection.

An inert split/splitless inlet weldment that minimizes absorption and degradation of active phosphorus pesticides was used. An Ultra inert liner (p/n 5190-3162) that also provides better inertness was selected for this study. The new FPD Plus with improvements in thermal zone control (independent emission block and transfer line temperatures) improves the detection sensitivity.

Organophosphorus pesticide standard and spiked water samples were analyzed. The RSD% was better than 2.8%. The linear correlation coefficient R^2 range was between 0.9996

and 0.9999, and recovery ranges were between 90.4% and 98.8%. All results are shown in Table 3. The chromatogram for organophosphorus pesticides standard at 0.05 mg/L concentration level is shown in Figure 5.

Samples were extracted by methylene chloride and dehydrated with anhydrous sodium sulfate. The excess solvent was removed by a rotary evaporator or Kuderna-Danish (KD) concentrator. Details can be found in Bureau of Environmental Protection of the People's Republic of China, "Water and Wastewater Monitoring Methods (Fourth Edition)" [3], or US Environmental Protection Agency, Method 614.1, "The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater" [4].

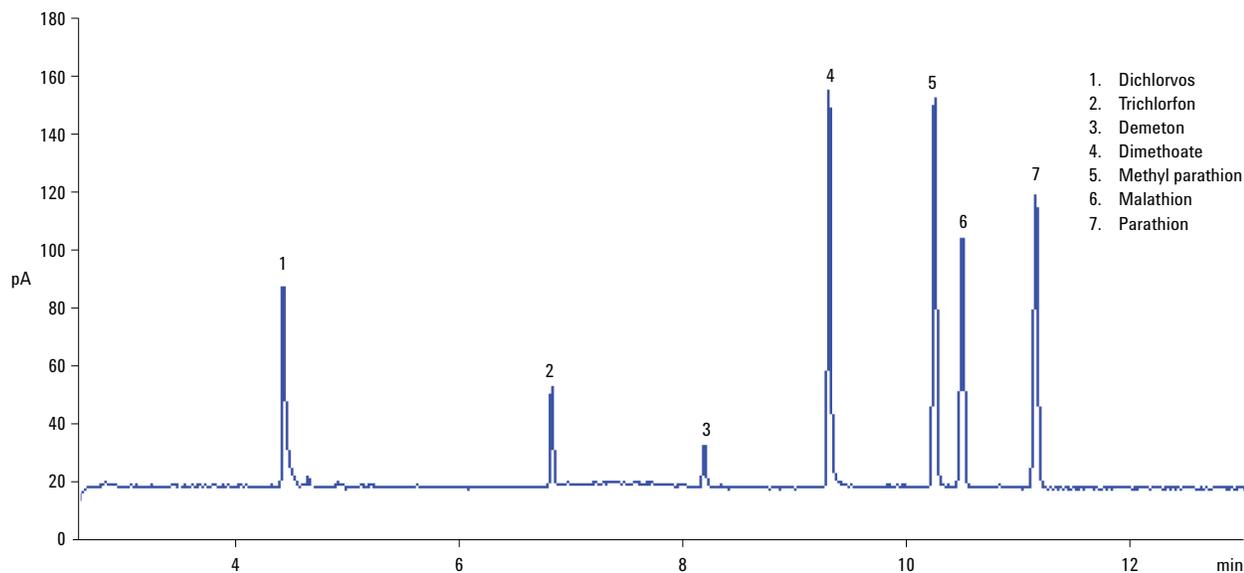


Figure 5. The chromatogram for organophosphorus pesticides standard at 0.05 mg/L concentration level.

Table 3. Analysis Results for Organophosphorus Pesticides

Compound name	Correlation coefficient R ²	RSD (0.05 mg/L, n = 6)		Spiked water (µg/L)	Recovery (%)
		Retention time	Peak area		
Dichlorvos	0.9997 (0.02–1 mg/L)	0.017	1.47	5	90.4
Trichlorfon	0.9996 (0.02–1 mg/L)	0.009	2.74	5	96.2
Demeton	0.9998 (0.02–1 mg/L)	0.007	2.48	5	98.8
Dimethoate	0.9999 (0.02–1 mg/L)	0.006	2.20	5	97.3
Methyl parathion	0.9999 (0.02–1 mg/L)	0.005	1.75	5	96.9
Malathion	0.9997 (0.02–1 mg/L)	0.006	1.73	5	95.3
Parathion	0.9998 (0.02–1 mg/L)	0.007	1.45	5	95.9

Conclusion

An Agilent 7890B gas chromatograph configured with three detectors (FID, ECD, and FPD) was used to measure volatile aromatic and halogenated hydrocarbons and organophosphorus pesticides in water. The system uses an unpurged CFT splitter and optimized headspace parameters to allow the simultaneous analysis of aromatic and halogenated hydrocarbons. The full inert split/splitless inlet including surface inlet weldment, shell, and liner minimizes the absorption and degradation of phosphorus-containing pesticides in contact with hot metal parts, and provides a higher response. A new FPD improves phosphorus sensitivity. The phosphorus sensitivity was 45 fgP/sec, improved from the previous generation PFD at 60 fgP/sec.

References

1. B. Kolb, and L.S. Ettre, "Static Headspace-Gas Chromatography: Theory and Practice", Second Edition, 2006, Hoboken, New Jersey: John Wiley & Sons, Inc. 349.
2. J. Bushey, "Thermal zone considerations for the Agilent 7697A headspace sampler", Agilent Technologies publication 5990-9892EN.
3. Bureau of environmental protection of the People's Republic of China, Water and Wastewater Monitoring Methods (Fourth Edition).
4. US Environmental Protection Agency, "Method 614.1 The Determination of Organophosphorus Pesticides in Municipal and Industrial Wastewater".

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc., 2013
Printed in the USA
August 5, 2013
5991-2787EN



Agilent Technologies