APPLICATION NOTE

Gas Chromatography/
Mass Spectrometry

Author:

Kira Yang

PerkinElmer Inc.
Shanghai, China

Determination of 2,4,6-Trichlorophenol in Water by Derivatization in Headspace and GC/MS

Introduction

Chlorophenols are by-products of the drinking water purification process and are also widely used as wood preservatives, herbicides and pesticides. They have a significant impact on human health and are regarded as refractory and highly toxic with the negative effects of "carcinogenesis, teratogenesis and mutagenesis". They are considered under the EPA and EU as Persistent Organic Pollutants (POP's) (Zhou, 1994) with O-chlorophenols, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol, also listed in monitoring programs "Sanitary standard for drinking water" in China (GB/T 5750.10, 2006)[1]. Several common methods for the determination of chlorophenols include solid-phase extraction-HPLC (Chao, 2008), derivatization gas chromatography (Tang, 2009 and GB/T 5750.10, 2006, EPA 8041A, 2000) and headspace solid phase microextraction (HSSPME) (GB/T 5750.10, 2006)[2,3,4,5]. The derivatization gas chromatography method is based on chlorophenols reacting with acetic anhydride in an alkaline aqueous solution to produce esters as shown in Figure 1. These esters are chromatographically stable with a higher vapor pressure than the parent phenol and since the esters are less polar they are more suitable to low level GC analysis. Once formed the esters are extracted by n-hexane for analysis by GC (Li, 2007)[6]. The hexane extraction is complicated, consumes significant quantities of organic solvent and is time/labor intensive.

PerkinElmer®
For the Better

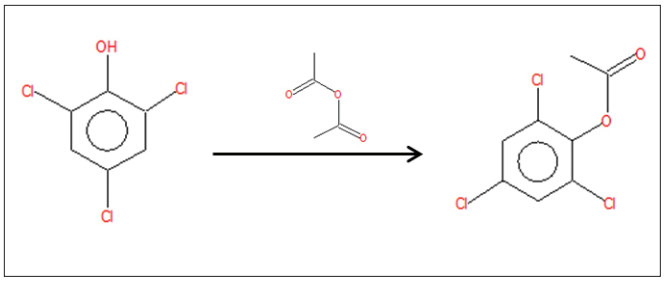

Figure 1. Production pathway.

The derivatization reaction mentioned above is performed in aqueous solution. Volatile materials can be extracted from water by heating the water to the proper temperature to establish a dynamic equilibrium based on the partition coefficients between solvent and headspace. The reaction products are esters with high volatility which are easily partitioned into the headspace vapor for analysis by gas shromatography/mass spectrometry (GC/MS).

In this study, 2,4,6-trichlorophenol in water was determined using a derivitization technique. The derivatization and extraction processes were performed automatically in the TurboMatrix™ HS-40 automatic headspace sampler and the reaction product, 2,4,6-trichlorobenzyl acetate, was detected by the PerkinElmer Clarus® S Q8 GC/MS. This new method is simple to operate with lower operational costs and significantly less laboratory waste.

Experimental

The PerkinElmer Clarus SQ 8 GC/MS operating in electron ionization mode with TurboMatrix HS-40 was used to perform this experiment using the conditions that are presented in Table 1.

The transfer line of the headspace device was connected directly to the injector port of the Clarus 680 GC. A PerkinElmer Elite 5 column (30 m x 0.25 mm x 0.25 um) was used.

The 2,4,6-trichlorophenol (100 µg/mL), was purchased from ANPEL Laboratory Technologies (Shanghai) Inc. Chromatographic grade methanol (HPLC grade, Fisher Scientific) was used for standard dilutions, to produce a range of concentrations required for the experiments. The calibration levels in this study are presented in Table 2. Analytic grade K^2CO^3 and acetic anhydride were purchased from Sinopharm Chemical Reagent Co. Ltd. The ultrapure water was produced by Mini-Q.

Five microliters of the calibration standard diluted according to Table 2 was added to 10 mL of K^2CO^3 aqueous solution (0.1 mol/L) in the 22 mL glass headspace vial. Then 0.5 mL of acetic anhydride was added as derivatization reagent. The vial was sealed immediately with the PTFE side of the septum facing toward the sample. Since the derivatization reaction occurs during vial thermostatting, there is no need to allow the vials to set at room temperature for the reaction to complete.

Results and Discussion

In this study, the derivatization and extraction happened in the headspace vials during the vial thermostatting step. The derivatization reaction is affected by temperature and time,

Table 2. Calibration points employed in this study.

Calibration level	1	2	3	4
Calibration standards concentration (µg/mL)	20.0	40.0	60.0	80.0

Table 1. Analytical parameters.

TurboMatrix HS-40					
Oven Temp (°C)	80	Thermostat Time (min)	20	Column Pressure (psi)	21
Needle Temp (°C)	90	Pressure Time (min)	1	Vial Pressure (psi)	21
Transfer line Temp (°C)	120	Injection Time (min)	0.1		
Clarus 680 GC					
Analytical Column	Elite-5 (30 m x 0.25 mm x 0.25 um)				
Carrier Gas (ml/min)	1.5	Injector Temp (°C)	250		
Split flow (ml/min)	20				
Oven Program	Temp (°C)	Hold Time (min)	Rate (°C/min)		
	60	2	10		
	210	0	20		
	250	3	-		
Clarus SQ 8 MS					
GC Inlet Line Temp (°C)	250	Solvent Delay (min)	3		
Ion Source Temp (°C)	250	Function Type	Scan and SIR		

therefore the thermostat time and oven temperature of the headspace sampler were investigated for optimum derivitization/extraction conditions.

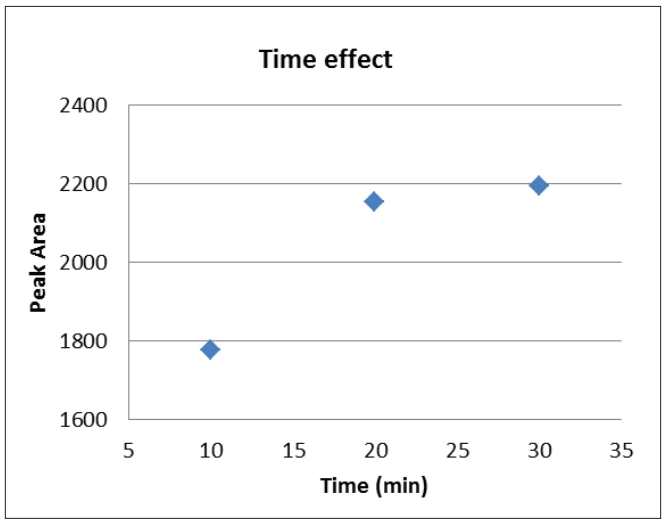

Figure 2. Relationship between thermostat time and peak area.

Effect of Thermostat Time

Three standards were heated at 80 °C for 10, 20 and 30 min, respectively. The increase in thermostat time from 10 to 20 min enabled greater reaction time for the derivitization and for the establishment of the partition between liquid and vapor phases with a significant increase in peak area. From 20 to 30 min, the increase of peak area was small. One can conclude that the derivatization reaction nearly reaches the thermodynamic equilibrium at 20 minutes which is in good agreement with previously reported results (Tang, 2009). In order to decrease analysis time, the thermostat time was set as 20 min.

Effect of Oven Temperature

The derivatiztion process has been reported at 60 °C (GB/T 5750.10, 2006) or room temperature (Tang, 2009) in the most common methods. The oven temperature of the headspace sampler has an effect on not only the process of derivatization but also the concentration of derivative product in the gas phase.

The relationship between oven temperature and peak area is shown in Figure 3. Three standards were heated for 20 min at 60 °C, 70 °C and 80 °C, respectively.

The peak area of 2,4,6-trichlorophenol acetate was increased with the increasing of oven temperature. To reduce the amount of acetic acid vapor that otherwise may interfere with the normal functionality of the filament in mass spectrometer, the oven temperature was set at 80 °C.

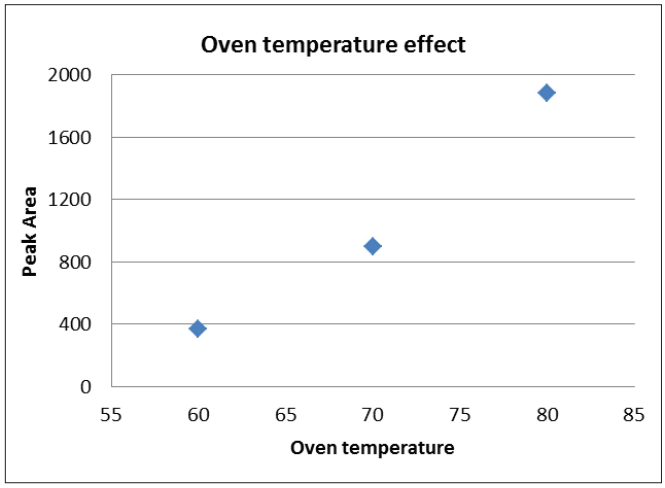

Figure 3. Relationship between oven temperature and peak area.

Chromatogram and Calibration Curve

The mass spectrum of 2,4,6-trichlorobenzyl acetate obtained from the 80 µg/mL spike of 2,4,6-trichlorophenol is shown in Figure 4 which is an excellent match with the NIST-library mass spectrum (Figure 5). The specific fragment ions at m/z 196, 198 and 43 were observed in the mass spectrum which can separate the target compound with other components using the SIR function.

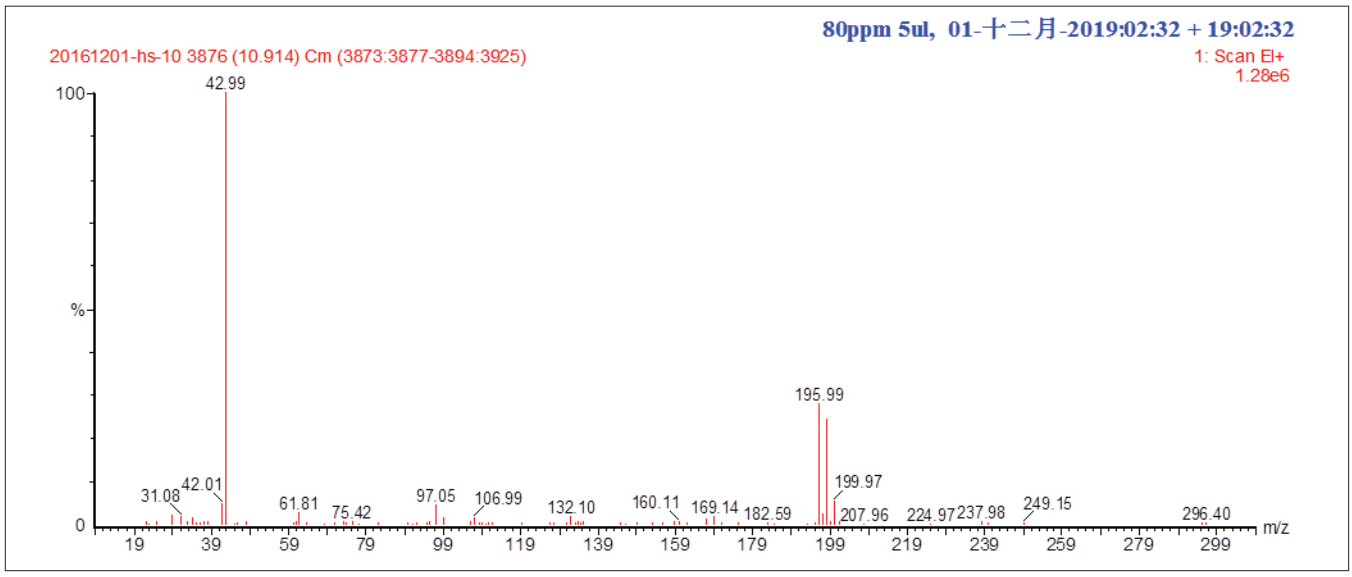

Figure 4. Expanded mass spectrum obtained from GC/MS analysis of 80 µg/mL 5 µL spike of 2,4,6-trichlorophenol in the potassium carbonate solution.

The SIR trace in Figure 6 shows 2,4,6-trichlorobenzyl acetate in the chromatographic run that selected ions at m/z 196 with high signal to noise (S/N = 1188.01). Linearity is demonstrated in Figure 7 using m/z 196 as quantified ion. The determination coefficient (r^2) was 0.99983 showing the reliability of the analysis.

Summary

In this study, a new method was developed for the determination of 2,4,6-trichlorophenol in water using a headspace sampler combined with GC/MS. The derivative product, 2,4,6-trichlorobenzyl acetate, was formed and extracted during the vial thermostatting step of the headspace method. This new method is simple to operate, has lower operational costs and produces less waste.

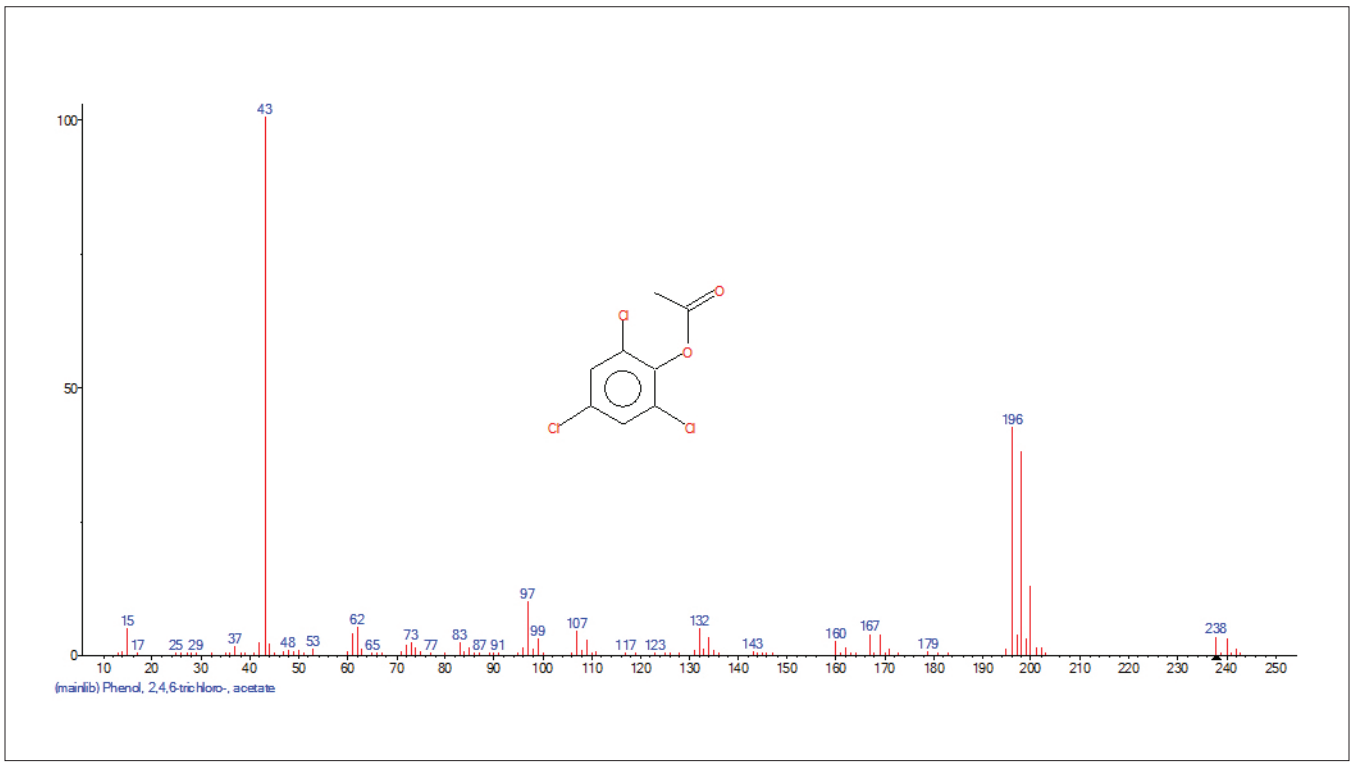

Figure 5. Expanded 2,4,6-trichlorobenzyl acetate mass spectrum obtained from NIST library.

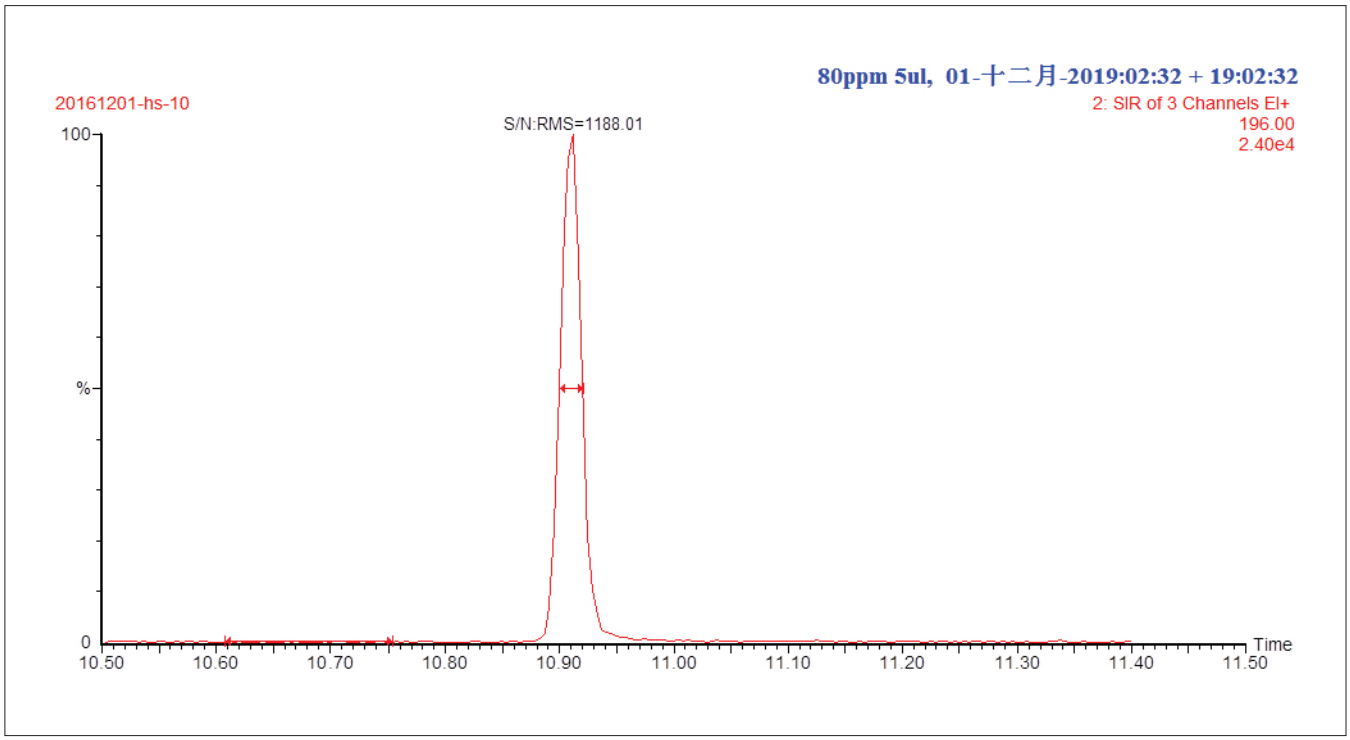

Figure 6. The selected ion chromatogram (m/z 196) of 80 µg/mL 5 µL spike of 2,4,6-trichlorophenol in the potassium carbonate solution with S/N 1188.01.

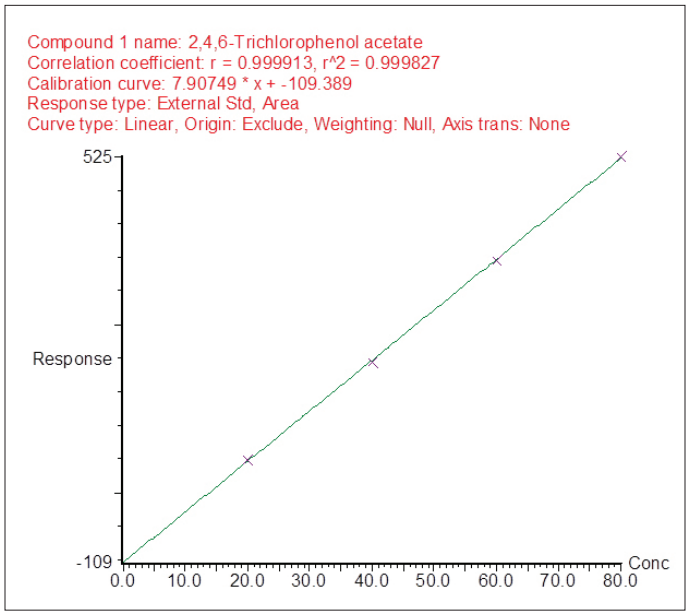

Figure 7. Calibration curve (20 - 80 µg/mL 5 µL spike of 2,4,6-trichlorophenol in 10 mL of the potassium carbonate solution).

Reference

1. Liangmo, Zhou, 1994. New technique of gas chromatography
2. Meng. Chao, Jianming. Liu, Ming. Chen, 2008. Determination of 2,4,6-trichlorophenol and pentachlorophenol in water by SPE-HPLC. Water Supply Technology.
3. Ting. Tang, Hao. Wang, Wusheng. Ma, Ping. Wu, 2009. Determination of chlorohpenols in water by derivatization gas chromatography. Chemical Engineer.
4. 2006. Sanitary standard for drinking water. GB/T 5750.10
5. 2000, Phenols by gas chromatrography, EPA 8041A
6. Mengyao. Li, Jinghui. Yang, Hui. Qian, 2007. The developments in the determination of pentachlorophenol. Analysis and Testing Technology and Instruments.

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

PerkinElmer®

For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

013558_01 PKI