

Determination of pesticide residues and toxins in drinking water by online SPE – high-performance liquid chromatography

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Keywords

Online SPE, pesticide residue,
drinking water

Goal

To describe a method for applying dual-gradient liquid chromatography in combination with solid-phase extraction to establish a simple, convenient, quick, and accurate method to determine the nine organic compounds in water.

Introduction

The analysis of organic compounds in drinking water offers many analytical challenges, ranging from water sampling to the ability to detect low target compound concentrations. Regulatory requirements need the testing of several analytes for drinking water like the Chinese standard GB/T 5479-2006¹ or the chemical contaminants list of the United States Environmental Protection Agency (US EPA)².

Often, conventional detectors do not meet the low detection limit requirements for trace detection; therefore, extensive sample pretreatment methods, such as bulk liquid extraction and offline solid phase extraction or post-column derivatization high performance liquid chromatography (HPLC), are used to reach the required detection limit. Traditional sample pretreatment typically results in large organic solvent consumption and large samples, which makes the pretreatment steps cumbersome, less accurate, and less precise.

With liquid chromatographic analysis, sample pretreatment is often a key factor in limiting the speed, sensitivity, and reproducibility. Online solid phase extraction (SPE) combined with HPLC is a simple, fast, and accurate sample pretreatment and analytical analysis. The Thermo Scientific™ UltiMate™ 3000 Dual Gradient LC system with semi-preparative split-loop autosampler can provide automated sample online enrichment, concentration, and matrix elimination up to 2.5 mL sample volume in default configuration. Compared with other pretreatment and detection methods, this option allows for high efficiency, simple operation, high sensitivity, and lower analysis costs.

Experimental

Equipment and software

The Thermo Scientific™ UltiMate™ 3000 Standard Dual LC system was used (Figure 1), which includes:

- Thermo Scientific™ UltiMate™ 3000 SRD-3600 Integrated Solvent and Degasser Rack (P/N 5035.9230)
- Thermo Scientific™ UltiMate™ 3000 DPG-3600SD Dual-Gradient Standard Pump (P/N 5040.0061)
- Thermo Scientific™ UltiMate™ 3000 WPS-3000TSL Semi-Preparative Split-Loop Thermostatted Well Plate Autosampler (P/N 5822.0028), equipped with a 2500 µL sample loop
- Thermo Scientific™ UltiMate™ 3000 TCC-3000RS Rapid Separation Thermostatted Column Compartment (P/N 5730.0000) with one 2p-6p switching valve
- Thermo Scientific™ UltiMate™ 3000 DAD-3000 Diode Array Detector (P/N 5082.0010), equipped with semi-analytical flow cell (stainless steel, 5 µL, P/N 6082.0200)
- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS)

Chromatographic conditions

Mobile phase	A: 0.05% phosphoric acid B: Water C: Acetonitrile		
Enrichment pump gradient	Time (min)	Enrichment pump (%B)	Enrichment pump (%C)
	0	95	0
	4	95	0
	4.1	0	0
	25	0	0
	28	95	0
	35	95	0
	43*	95	0
Analytical pump gradient	Time (min)	Analytical pump (B%)	Analytical pump (C%)
	0	70	30
	5	70	30
	6	50	50
	8	50	50
	10	40	60
	13	40	60
	14	0	60
	15	0	75
	19.5	0	75
	22.5	0	100
	26	0	100
	35	70	30
	43*	70	30
Valve position	Time (min)	Valve position	Status
	0	1–2	Extraction
	4	6–1	Elution/separation
	25	1–2	Cleaning/equilibration
Injection volume	2.5 mL		
Flow rate	0.7 mL/min		
Temperature	40 °C		
UV wavelength	210 nm, 220 nm, 238 nm, 280 nm		

*Note: An additional 5–8 min was added at the end of the instrument method to allow for proper column re-equilibration.

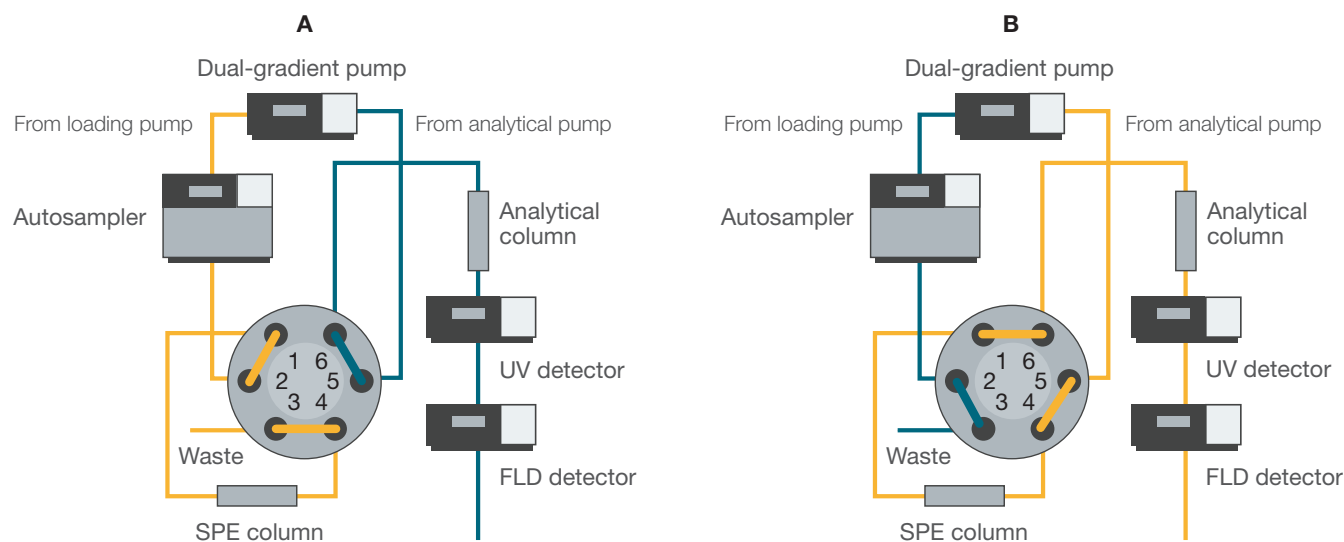


Figure 1. The UltiMate 3000 Dual-Gradient pump with autosampler and fluorescence detector connected to a six-port switching valve to load, clean, and extract the sample on the solid phase extraction column (A), followed by elution and separation on an analytical column (B)

Consumables

- Thermo Scientific™ Acclaim™ Polar Advantage II LC analysis column (3 μm, 3 × 150 mm, P/N 063705)
- Thermo Scientific™ Acclaim™ Polar Advantage II LC enrichment column (3 μm, 3 × 33 mm, P/N 066276)
- Eluents and standard compounds were purchased based on the Chinese standard GB/T 5749-2006 from the Ministry of Health of the People’s Republic of China.¹

Sample preparation

Water samples were filtered over a 0.22 μm pore size nylon membrane filter. Filtered samples were then transferred into sample vials for direct sample injection or treated with organic solvent, as described below.

For the determination of microcystins-LR, carbaryl, atrazine, carbofuran, 2,4,6-trichlorophenol, and chlorothalonil, water samples can be analyzed immediately after filtering with no further treatment.

Due to the lower solubility of deltamethrin and pentachlorophenol in water, recovery rate and sensitivity was significantly improved by adding acetonitrile to the sample after filtering. By using recovery rate as an indicator, 25% acetonitrile/water solution was found to be the optimal solvent to analyze deltamethrin and pentachlorophenol. For the results shown in this work, the tested sample matrix contained 25% acetonitrile.

Standard solution preparation

Standard substances were dissolved in acetonitrile and then diluted to the calibration standard concentrations with acetonitrile/water (25:75, v/v).

Results and discussion

Standard

A standardized mixture containing all nine targeted compounds was analyzed using the chromatographic conditions described above. The results show that eight of the targeted compounds can be well separated with the appropriate peak resolution to meet the Chinese standard GB/T 5749-2006 requirements with UV detection (Figure 2). The large peak observed at 12 minutes is enriched contaminants of loading pump mobile phase.

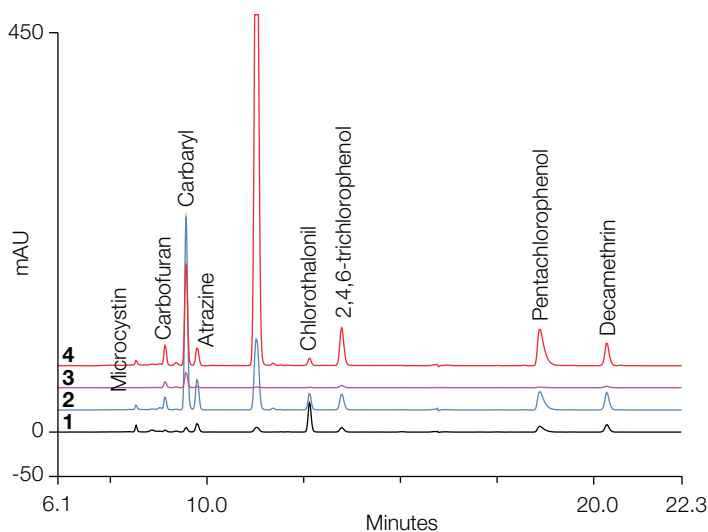


Figure 2. Chromatogram of peaks observed with UV detection at various wavelengths (1: 238 nm; 2: 220 nm; 3: 280 nm; 4: 210 nm)

Sensitivity and linearity

Good linearity was obtained with a linear correlation coefficient $r > 0.999$.

The limit of detection (LOD) was estimated from signal and noise using the formula $LOD = 3 (S/N)$. The lowest LOD for the eight compounds was estimated between 0.03 and 0.75 ng/L; the results show that the LODs for the chemical compounds meet the requirements for the Chinese standard.

Tables 1 and 2 list the specific linearity and limit of detection data.

Water sample analysis

This method was applied to the analysis of collected surface water and source water samples. All target chemical compounds were below the limit of detection. Therefore, to determine the recovery rate of the method, the water samples were spiked with standards (low and high concentrations) and analyzed. The obtained recovery rates of the chemical compounds were 92.4–125% with RSD < 5%. See Tables 3 and 4 for the results.

Table 1. Linearity and limits of detection for microcystins-LR, carbaryl, atrazine, carbofuran, chlorothalonil, and 2,4,6-trichlorophenol

Chemical compound	Wavelength (nm)	Correlation coefficient	Injected standard concentration (µg/L)	LOD (µg/L)	LOQ (µg/L)
Microcystins-LR	238	0.9990	0.18–9.00	0.05	0.17
2,4,6-trichlorophenol	210	0.9995	0.40–30.00	0.12	0.40
Atrazine	220	1.000	0.10–15.00	0.03	0.10
Carbaryl	220	1.000	0.20–30.00	0.06	0.20
Carbofuran	280	0.9995	0.40–30.00	0.12	0.40
Chlorothalonil	238	1.000	0.20–15.00	0.05	0.17

Table 2. Linearity and limits of detection for decamethrin and pentachlorophenol

Chemical compound	Wavelength (nm)	Correlation coefficient	Injected standard concentration (µg/L)	LOD (µg/L)	LOQ (µg/L)
Decamethrin	238	0.9995	2.50–250.00	0.75	2.50
Pentachlorophenol	210	0.9995	0.5–12.00	0.15	0.50

Table 3. Recovery results of microcystins-LR, and 2,4,6-trichlorophenol, atrazine, carbaryl, carbofuran, and chlorothalonil

Chemical compound	Addition amount (µg/L)	Measured amount (µg/L)	Recovery rate (%)	RSD (%)
Microcystins-LR	0.90	1.11	123.64 ± 0.02	0.01
	5.40	4.97	92.12 ± 0.01	0.01
2,4,6-trichlorophenol	2.00	1.99	99.23 ± 0.16	0.16
	12.00	12.15	101.26 ± 0.25	0.25
Atrazine	1.00	1.03	102.99 ± 0.60	0.58
	6.00	6.06	100.92 ± 0.16	0.16
Carbaryl	2.00	2.02	101.13 ± 0.90	0.90
	12.00	11.21	93.42 ± 2.44	2.60
Carbofuran	2.00	1.88	94.27 ± 0.30	0.32
	12.00	11.41	95.12 ± 0.53	0.56
Chlorothalonil	1.00	0.99	98.66 ± 0.22	0.22
	6.00	6.03	100.54 ± 0.14	0.14

Table 4. Recovery results of decamethrin and pentachlorophenol

Chemical compound	Addition amount (µg/L)	Measured amount (µg/L)	Recovery rate (%)	RSD (%)
Decamethrin	25.00	24.31	97.78 ± 4.50	4.60
	150.00	142.81	95.21 ± 4.75	4.99
Pentachlorophenol	2.00	1.85	92.73 ± 4.67	5.00
	12.00	11.09	92.43 ± 3.37	3.65

Conclusion

This application note describes a method for applying dual-gradient liquid chromatography in combination with online solid-phase extraction to establish a simple, convenient, quick, and accurate method to determine the nine organic compounds in water. This method achieves pre-concentration by online sample extraction and subsequent analysis for water samples, while avoiding tedious sample preparation, and greatly saves time and volume of sample used while maintaining good reproducibility. It is applicable for determining microcystins-LR, carbaryl, atrazine, carbofuran, chlorothalonil, 2,4,6-trichlorophenol, pentachlorophenol, and deltamethrin in water.

Reference

1. Standard Test Method for Standard of Domestic Drinking Water [S]. China Standard Press, 2006, Ministry of Health of the People's Republic of China GB / T 5750-2006.
2. US EPA Chemical Contaminants - CCL 4 <https://www.epa.gov/ccl/chemical-contaminants-ccl-4>

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