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Application News

Polarity-Extended Liquid Chromatography; Nexera™ XS Liquid Chromatograph Mass Spectrometry LCMS-8050 Series

Rapid Screening of 501 Emerging Contaminants in Water Using Polarity-Extended Liquid Chromatography-Mass Spectrometry

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User Benefits

- Polarity-Extended Liquid Chromatography combines hydrophilic interaction chromatography and reversed-phase chromatography to achieve simultaneous analysis of polar and weakly polar compounds.
- This method can detect 501 emerging contaminants, offering a broad scope in terms of both quantity and variety.
- The water sample is concentrated using freeze-drying method, effectively recovering both polar and non-polar compounds are recovered well.

■ Introduction

In recent years, water pollution has become increasingly serious, and the problem of emerging pollutants in water has attracted much attention. Traditional analytical methods for emerging pollutants mainly focus on 1-2 categories of emerging pollutants and pay less attention to strongly polar pollutants. The Polarity-Extended Liquid Chromatography, through patented technologies such as polarity splitting, online dilution, and dual gradients, combines a Hilic column (first dimension) and a C18 column (second dimension), which can broaden the polarity analysis range of compounds and achieve simultaneous analysis of polar and weakly polar compounds. Fig. 1 shows the Polarity-Extended Liquid Chromatography-Mass Spectrometry System.

In this paper, a method for rapid screening of 501 emerging pollutants was established by using Shimadzu's Polarity-Extended Liquid Chromatography-Mass Spectrometry System. This method solves the problem of simultaneous analysis of strong and weak polar pollutants.

■ Sample Preparation

Take 50 mL of environmental water sample into a 50 mL centrifuge tube, add 50 mg of EDTA, mix well, and place it in a -80°C refrigerator for overnight freezing. Put the sample in a freeze dryer and dry it in vacuum until the sample is evaporated to dryness. Add 10 mL of methanol (containing 0.1% formic acid) solution and shake for 2 minutes. Blow the sample to nearly dry with nitrogen at room temperature. Add 1 mL of 50% methanol aqueous solution, shake for 2 minutes, pass through a 0.22 μm filter membrane, and measure on the instrument.

■ Analytical Condition

The analytical conditions for HPLC and MS are shown in Table 1. The time program of two dimentions are shown in Table 2 and 3. Flow diagram of Polarity-Extended Liquid Chromatography System are shown in Fig. 2.

Fig. 1 Polarity-Extended Liquid Chromatography-Mass Spectrometry System

Table 1 Analysis Conditions of PELC and LCMS-8050 Series

System	: Polarity-Extended Liquid Chromatography
Columns	: 1st dimention: Waters Cortecs HILIC(150 mm×2.1 mm I.D., 2.7 μm) 2nd dimention: Shim-pack GIST-HP C18-AQ (150 mm×2.1 mm I.D., 3 μm)
Mobile phase	: A: 0.1% FA, B: Acetonitrile(1st dimention), A: 2mM ammonium acetate aqueous solution (containing 0.01% formic acid), B: Acetonitrile(2nd dimention),
Column Temparature	: 40 ˚C
Injection volume	: 5 μL
FCV Valve Position	: 0 (0 min) → 1 (1.6 min) →0 (10 min)
System	: LCMS-8050 Series (ESI)
Nebulizing gas	: 3 L/min
Drying gas	: 10 L/min
Heating gas	: 10 L/min
DL temp	: 200 ˚C
Heat block temp	: 400 ˚C
Interface temp	: 300 ˚C

Table 2 Time program of 1st dimention liquid chromatography

Time(min)	Unit	B%	Flow rate (mL/min)
0.00	Pump	97	0.4
2.50	Pump	97	0.4
3.50	Pump	60	0.4
6.50	Pump	55	0.4
6.80	Pump	35	0.4
9.50	Pump	20	0.4
9.60	Pump	97	0.4
28.00	Controller	Stop	

Table 3 Time program of 2nd dimention liquid chromatography

Time(min)	Unit	B%	Flow rate (mL/min)
0.00	Pump	5	0.3
1.70	Pump	5	0.3
1.80	Pump	5	1.5
9.70	Pump	5	1.5
9.80	Pump	5	0.3
10.00	Pump	5	0.3
10.20	Pump	45	0.3
22.50	Pump	65	0.3
24.50	Pump	95	0.3
26.50	Pump	95	0.3
26.60	Pump	5	0.3
28.00	Controller	Stop	

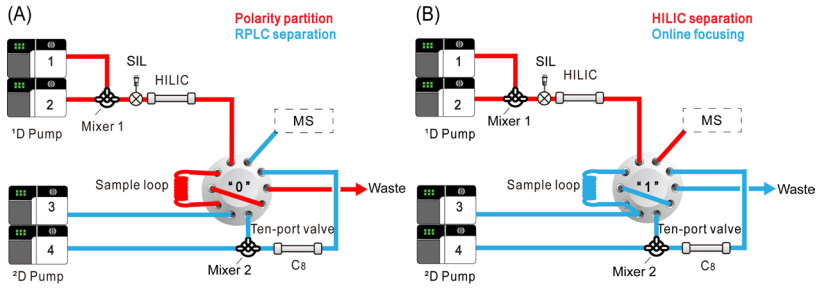

Fig. 2 Flow diagram of Polarity-Extended Liquid Chromatography System[1)]

■ Chromatograms of 501 compounds

Fig. 3 shows the chromatograms of 501 compounds in this method.

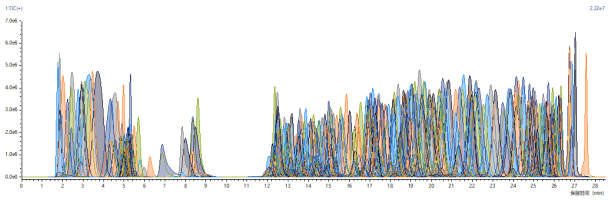

Fig. 3 Chromatograms of 501 compounds

■ Characteristics of PELC in this topic

Retention of strongly polar compounds

Traditional analytical ideas for emerging pollutants use C18 columns for analysis. However, the separation ability of C18 columns for strongly polar target compounds is relatively weak. These substances hardly have any retention on C18 columns, and problems such as solvent effect and matrix effect are prone to occur. In this method, a Hilic column is first used, which has a better retention and separation effect on strongly polar compounds. Then, medium-polar and weak-polar compounds are introduced into the C18 column in the second dimension for separation, realizing the full separation of strongly polar to weak - polar compounds. Fig. 4 shows MRM of some strongly polar compounds.

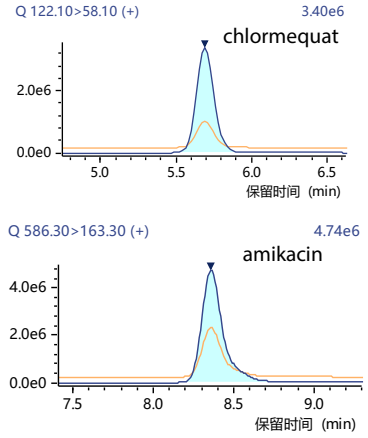

Fig. 4 MRM of some strongly polar compounds.

Coverage of types of emerging pollutants

This method collects 501 emerging pollutants, including PFASs, PPCPs, hormones, preservatives, insecticides, fungicides, organophosphorus flame retardants, anilines, herbicides, plant growth regulators, etc. The propotion of number of each type of pollutants in this method is listed in Fig. 5.

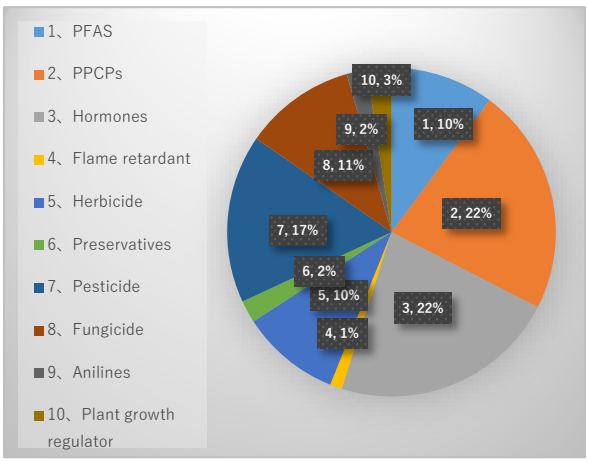

Fig. 5 The proportion of the number of each type of pollutant in this method

Typical chromatograms of high concern substances

This method includes 46 PFASs and 112 PPCPs. The chromatograms of PFASs and PPCPs are as follows. Fig. 6 shows the chromatograms of PFASs and PPCPs.

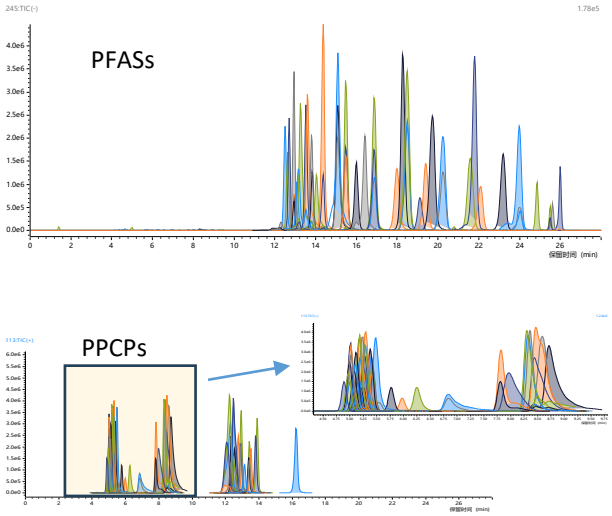

Fig. 6 Chromatogram of PFASs and PPCPs

■ Method validation

Linearity

External standard method was used for quantification. The linear correlation coefficient R of the calibration curves of 501 compounds was ≥0.994.

Repeatability

Two concentration levels of high and low concentration points were selected for repeatability investigation. Six consecutive injections were made. For the vast majority of compounds, the RSD of peak area was less than 10%, and the RSD of retention time was less than 0.3%. Detailed results are shown in Fig. 7 and Fig. 8.

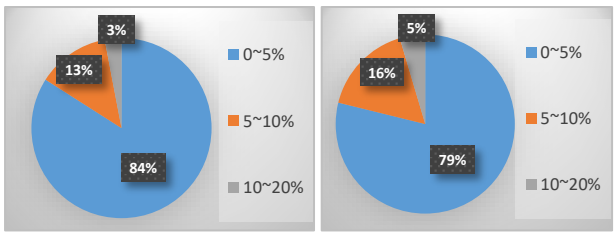

Fig. 7 RSD Distribution Diagram of Peak Area for Repeated Injections (Left: High Concentration, Right: Low Concentration)

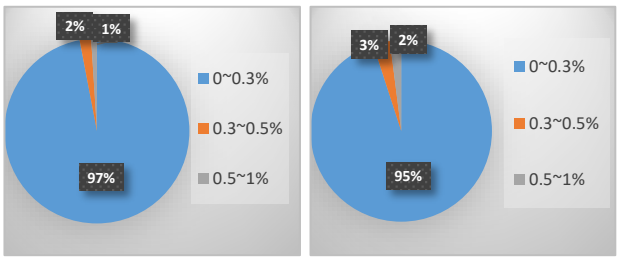

Fig. 8 RSD Distribution Diagram of Retention time for Repeated Injections (Left: High Concentration, Right: Low Concentration)

Recovery

A mixture of emerging pollutant standard substances was added to pure water samples to investigate the recovery rate during the screening process. Under the current pretreatment method, 76% of the compounds have a recovery rate better than 50%.

Analysis of actual samples

Tap water and sewage were selected respectively. After the water samples were processed, they were analyzed on the instrument. The screening results in Fig. 9 show that pollutants were detected in both tap water and sewage samples.

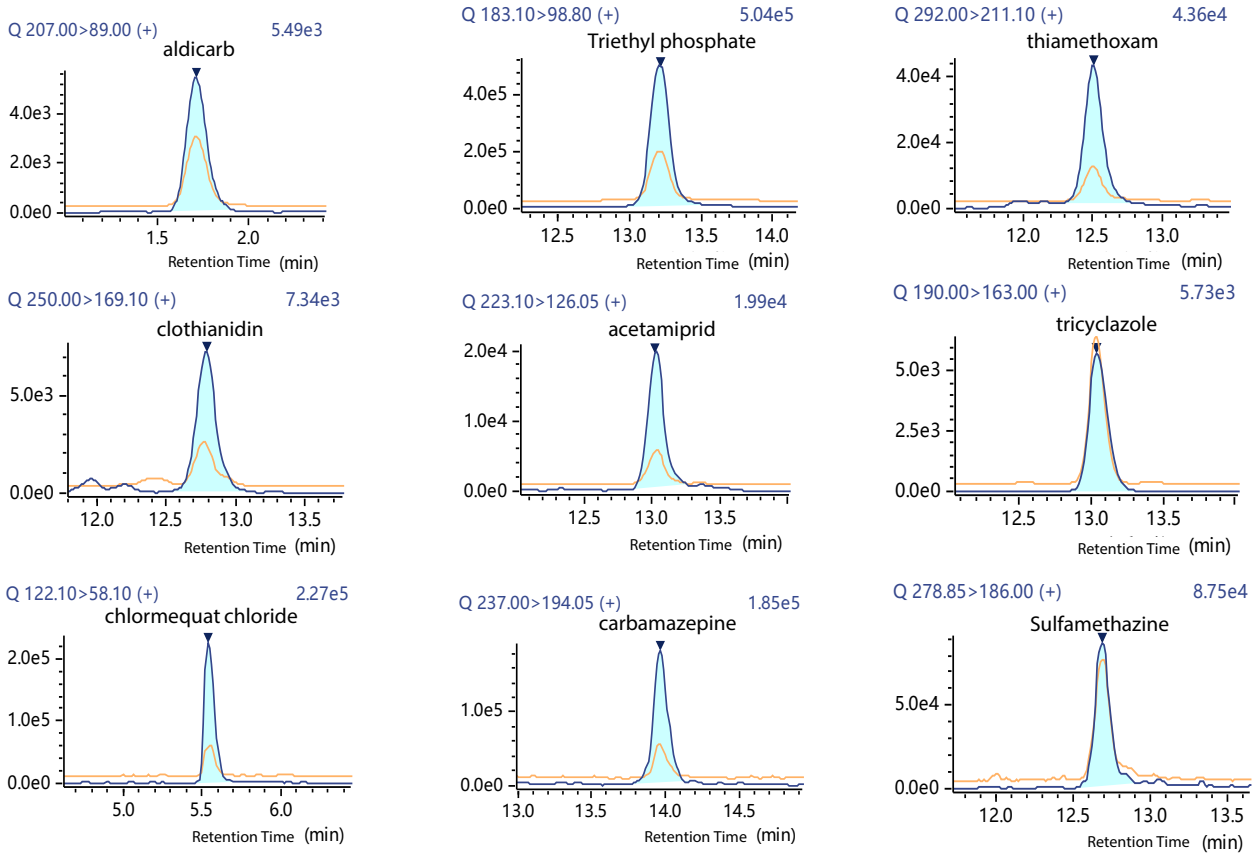

Fig. 9 Pollutants detected in tap water and sewage

■ Conclusion

In this study, a method for detecting emerging pollutants in water by combining the Polarity-Extended Liquid Chromatography and LCMS - 8050 series coupling system was established. This method combines hydrophilic interaction chromatography and reversed - phase chromatography to achieve the simultaneous separation of polar and non - polar compounds with a single injection. The detection of 501 emerging pollutants was achieved within 28 minutes. The linearity and repeatability of the method meet the quantitative requirements. After pretreatment operations such as freeze - drying, re - dissolution, and nitrogen blowing of the samples, the recovery rates for most compounds were satisfactory. This method has been successfully used for the rapid screening of new pollutants in tap water and sewage. The combination of Polarity-Extended Liquid Chromatography and mass spectrometry enables the one-injection analysis of compounds with different polarities without significantly increasing analysis time, making it suitable for the rapid screening of emerging pollutants in water.

<References>

1) Rui Guo, Qisheng Zhong, Jiaqi Liu, Peiming Bai, Zongpeng Wang, Jieling Kou, Polarity-extended liquid chromatography-triple quadrupole mass spectrometry for simultaneous hydrophilic and hydrophobic metabolite analysis. Analytica Chimica Acta, Volume 1277, 2023, 341655

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