

Comprehensive Characterization of Organic Pollutants in Wastewater from Acrylic Fiber Production

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Section A: Experimental Procedure Details

1. Sample Pretreatment Methods for Conventional Water Quality Index Testing

Transfer 7.6 mL of ultrapure water and 0.4 mL of the water sample into a 10 mL centrifuge tube, and mix thoroughly by vortexing. Dilute the test water sample 20-fold and adjust the pH to below 2 using analytical-grade hydrochloric acid. Filter the solution through a 0.22 μm membrane filter into a 1 mL vial, and store it for subsequent instrumental analysis.

2. Full Two-Dimensional Gas Chromatography-Tandem Mass Spectrometry (GC $\times$ GC-QTOF)

(1) Purge and Trap Procedure

The purge and trap procedure consists of three sequential steps: purging, desorption, and baking. The operational conditions for purge and trap were set according to the manufacturer's recommended parameters for the instrument, as specified in Table S1. A 50 mL water sample, pre-filtered through a 0.22 μm membrane to remove particles and other impurities, was introduced into the purge tube. During the experiment, a blank test was conducted in parallel by replacing the wastewater sample with an equal volume of ultrapure water. The entire procedure was repeated identically for the blank. In subsequent data analysis, any compounds detected in the blank must be subtracted from the sample results to ensure accurate quantification.

Table S1. Purge and Trap Conditions of GC $\times$ GC-QTOF

Purge Flow Rate	40 mL/min
Purge Temperature	20 $^{\circ}\text{C}$
Purging Time	11 min
Desorption Temperature	250 $^{\circ}\text{C}$
Desorption Time	2 min
Baking Temperature	280 $^{\circ}\text{C}$
Baking Time	2 min

(2) Solid-Phase Extraction Procedure

The solid-phase extraction procedure consists of four sequential steps: activation of the extraction cartridge, sample loading, rinsing, and elution. Two commonly used sorbent materials—C18 and HLB cartridges—were selected for comparison. Prior to extraction, the water sample was filtered through a 0.22 μm bottle-top filter to remove particulate matter. The experimental setup is illustrated in Figure S1(a).

① C18 Solid-Phase Extraction

A 10 mL volume of methanol was passed through the cartridge under gravity at a flow rate of 1 mL/min to activate it, followed by equilibration with 10 mL of ultrapure water at the same flow rate for the C18 solid-phase extraction cartridge. Subsequently, 200 mL of the water sample, pre-filtered by suction filtration, was loaded onto the C18 cartridge at a flow rate of 5 mL/min. During loading, the control valve was adjusted to maintain the liquid level above the sorbent bed no higher than 1 cm and to keep the applied pressure at approximately 8 inHg, ensuring that the sample flow rate through the column remained consistent with the set loading rate. After sample loading, the cartridge was rinsed with 10 mL of ultrapure water at 5 mL/min. The column was then dried under vacuum for 10 minutes, and analytes were eluted with 10 mL of methanol at a flow rate of 5 mL/min into a 10 mL centrifuge tube. This procedure follows the protocol described in Reference [24].

② HLB Solid-Phase Extraction

Activate the HLB cartridge with 10 mL of methanol at a flow rate of 1 mL/min, followed by equilibration with 10 mL of 0.01 M hydrochloric acid at the same flow rate. After suction filtration, 200 mL of the water sample was loaded onto the cartridge at a flow rate of 5 mL/min. The cartridge was then rinsed with 10 mL of 0.01 M hydrochloric acid at 5 mL/min, and analytes were eluted with 10 mL of methanol at a flow rate of 5 mL/min into a collection tube. This procedure follows that described in Reference [25].

The eluent was purged gently under a stream of nitrogen until approximately 0.3 mL remained. It was then diluted to 2 mL with n-hexane, vortexed thoroughly, allowed to stand for phase separation, and approximately 1 mL of the upper organic layer was transferred through a 0.22 μ m nylon membrane filter into a chromatographic vial for instrumental analysis. A blank test was conducted in parallel by replacing the wastewater sample with an equal volume of ultrapure water. The entire procedure was repeated identically for the blank. In subsequent data evaluation, any compounds detected in the blank must be subtracted from the sample results to ensure accurate identification and quantification.

(3) Vacuum Freeze-Drying Procedure

Transfer 20 mL of the water sample, pre-filtered through a 0.22 μ m membrane filter, into a centrifuge tube for vacuum freeze-drying. The experimental setup is illustrated in Figure S1(b). After freeze-drying, the residue was completely dissolved in 2 mL of n-hexane and vortexed thoroughly. Following phase separation, 1 mL of the upper organic layer was transferred and filtered through a 0.22 μ m nylon membrane into a chromatographic vial for analysis. During the experiment, 1 mL of n-hexane was used as a blank control to account for and eliminate potential background interference.

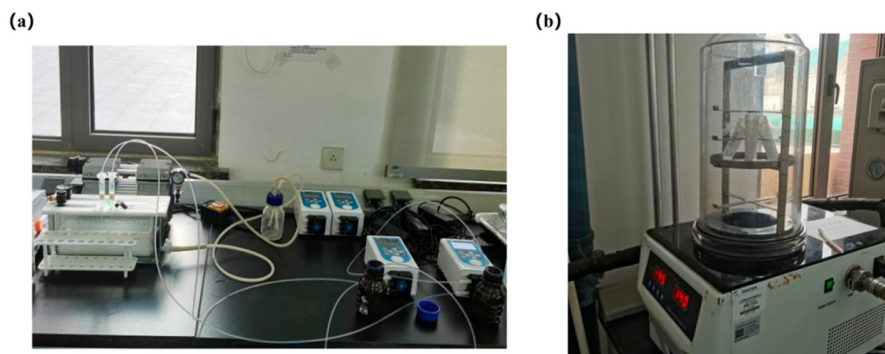


Figure S1. (a) Solid-phase extraction device (b) vacuum freeze-drying device

(4) All GC×GC Analytical Conditions

Helium was used as the carrier gas. A one-dimensional HP-5 weakly polar column (60 m × 0.25 mm × 0.25 μm) and a two-dimensional DB-17 moderately polar column (2 m × 0.25 mm × 0.25 μm) were employed. The column flow rate was set at 1.2 mL/min, and split injection was performed with a split ratio of 50:1. The injector temperature was maintained at 300 °C. The initial oven temperature was 50 °C, followed by a programmed temperature ramp from 50 °C to 300 °C at 6 °C/min, held for 5 min, resulting in a total run time of 46.67 min. The transfer line temperature was kept at 300 °C, and the modulation period was 6 s.

(5) Mass Spectrometry Conditions

The electron ionization energy was set at 70 eV. Full scan mode was employed with a mass range of 50–450 m/z and an acquisition rate of 50 spectra per second. The ion source was operated in electron ionization (EI) mode at 200 °C. The quadrupole temperature was maintained at 150 °C, and a solvent delay of 3 min was applied.

3. Ultra-Performance Liquid Chromatography-Tandem Mass Spectrometry (UPLC-Q-Orbitrap)

The sample pretreatment procedure for UPLC-MS/MS was essentially identical to that used for GC×GC-MS/MS, including solid-phase extraction steps such as cartridge activation, sample loading, rinsing, and elution, as well as the vacuum freeze-drying process. For detailed procedures, refer to sections (2) and (3) above. After solid-phase extraction, the eluent was concentrated under a stream of nitrogen and reconstituted in 1 mL of methanol. A blank test was performed by replacing the wastewater sample with an equal volume of ultrapure water. Freeze-dried samples were dissolved in 2 mL of methanol, and 1 mL of methanol was used as a procedural blank to account for and eliminate background interference. All other steps followed the same protocol.

Chromatographic conditions: A Thermo Scientific amide column (2.1 mm × 10 cm × 2.6 μm) was used. Mobile phase A consisted of 10% acetonitrile and 90% H₂O; mobile phase B consisted of 90% acetonitrile and 10% H₂O. The flow rate was set at 0.2 mL/min.

Mass spectrometry conditions: An electrospray ionization source (ESI) was employed in full-

scan mode (Full-MS) with a resolution of 35,000 and a scan range of m/z 80–1200.

4. Fourier Transform Infrared Spectroscopy (FTIR): Sample Pretreatment and Measurement Conditions

The water samples were lyophilized using a vacuum freeze dryer to obtain a solid powder. The dried samples were analyzed in attenuated total reflectance (ATR) mode using a diamond ATR accessory, with background subtraction performed prior to measurement. Spectra were recorded over a scanning range of 4000–600 cm^{-1} .

5. UV₂₅₄: Sample Pretreatment and Measurement Conditions

Take 3 mL of water samples that have been filtered through a 0.22 μm filter membrane, use ultrapure water as the reference, and set the sample cell as a 1 cm quartz cuvette. Measure the absorbance of the samples at a wavelength of 254 nm.

6. Three-Dimensional Fluorescence Spectroscopy: Sample Pretreatment and Measurement Conditions

The water sample was filtered through a 0.22 μm membrane filter and directly introduced into the instrument for analysis. The excitation wavelength (Ex) range was set from 220 to 450 nm, and the emission wavelength (Em) range from 280 to 550 nm. The response time was set to automatic, the slit width was 5 nm, and ultrapure water was used as the blank control.

7. NMR spectrometer: Sample Pretreatment and Measurement Conditions

Transfer 30 mL of the water sample, pre-filtered through a 0.22 μm membrane filter, into a centrifuge tube for vacuum freeze-drying [19]. After freeze-drying, record the mass of the solid residue for each sample. Based on the TOC values of different water samples, estimate the amount of residue to be weighed (no precise quantification required). Considering solubility and cost, deuterated water was selected as the solvent. The solid residue was dissolved in 0.5 mL of deuterated water. If any undissolved material remained, the solution was filtered through a syringe filter before being transferred to a 5 mm NMR tube for ^1H NMR analysis.

Instrument conditions: Nuclear magnetic resonance frequency: 600 MHz; Magnetic field strength: 14 tesla; Cavity diameter: 54 mm; ^1H sensitivity $\geq 900:1$ (0.1% ethylbenzene in CDCl_3); 5 mm Z-gradient broadband two-in-one BBO probe; Number of scans: 16.

Section B: Test Results Information

The results of conventional water quality indicators for the four types of wastewater examined in this study are presented in Table S2.

Table S2. Test Results of Conventional Water Quality Indicators

Number	Sample Name	pH	EC (ms/cm)	TOC (mg/L)	TN (mg/L)
1	Acrylonitrile mixed wastewater	6.87	0.65	163.4	69.4
2	Acrylic fiber polymerization wastewater	5.70	3.05	399.4	195.6
3	Acrylic fiber spinning wastewater	6.54	5.30	210.0	136.4
4	Acrylic fiber mixed wastewater	7.22	4.50	207.2	113.8

The three-dimensional fluorescence spectral partitioning of DOM is shown in Figure S2 and Table S3.

Table S3. Three-Dimensional Fluorescence Spectral Partitioning

region	I	II	III	IV	V
Ex/Em	<250/280-320	<250/320-400	<250/400-550	250-450/280-400	250-450/400-550
Peak category	Tyrosine-like peaks	Aromatic protein peaks (tryptophan type)	Fulvic acid-like peaks	Aromatic protein analogues, microbial by-products	Humic acid-like peak

The sampling volumes for the four types of wastewater during the ^1H NMR analysis are presented in Table S4.

Table S4. Estimation of Sampling Volume for Hydrogen Spectrum

Number	Sample Name	EC($\mu\text{s}/\text{cm}$)	Carbon Content /30mL(mg)	Total Mass after Freeze-Drying (mg)	Sampling Volume (mg)
1	Acrylonitrile mixed wastewater	650	4.902	3	3
2	Acrylic fiber polymerization wastewater	3050	11.982	27	7
3	Acrylic fiber spinning wastewater	5300	6.300	74	25
4	Acrylic fiber mixed wastewater	4500	6.216	50	15

The classification results of hydrogen spectrum signal peaks for the four types of wastewater are presented in Tables S5–S8.

Table S5. Test Results of Acrylonitrile Mixed Wastewater

Chemical Shift (ppm)	Potential H Type	Percentage (%)	Relative Peak Area	References
>6.0	Ar-H	/	/	0
5.06, 4.98	C=CH	12.76	2.22	00
3.77	CH-O	0.75	0.13	0
3.71, 3.69, 3.65	CH-O	2.24	0.39	0
3.57	CH-O	12.64	2.20	0
3.42	CH-O	4.02	0.70	0
3.22, 3.16	CH-O	13.45	2.34	0
3.06	CH-N	7.87	1.37	00
2.87, 2.79	CH-N, HC-C-O	11.90	2.07	0
2.70	CH-N, HC-C-O	2.41	0.42	0
2.53	CH-N, HC-C-O	7.64	1.33	0
2.42	CH-N, HC-C-O	1.21	0.21	0
2.10	C=C-C-H, O=C-C-H	10.46	1.82	0
1.85	C=C-C-H, HC-C-O, HC-C-N	12.01	2.09	0
1.30	R-CH ₂	0.63	0.11	0

Table S6. Test Results of Acrylic Fiber Polymerization Wastewater

Chemical Shift (ppm)	Potential H Type	Percentage (%)	Relative Peak Area	References
>8.0	Ar-H	/	/	0
5.05, 4.97	C=CH	8.03	2.09	00
3.98	CH-O	1.23	0.32	0
3.84, 3.76	CH-O	13.64	3.55	0
3.70, 3.68	CH-O	1.08	0.28	0
3.58	CH-O	10.10	2.63	0
3.20, 3.19	CH-O	8.84	2.30	0
3.17, 3.16	CH-O	5.84	1.52	0
3.14, 3.13	CH-O	8.18	2.13	0
3.10, 3.09	CH-N	2.04	0.53	00
3.01, 2.99	CH-N	1.96	0.51	00
2.88, 2.86, 2.85, 2.83, 2.82	CH-N, HC-C-O	12.37	3.22	00
2.11	C=C-C-H, O=C-C-H	12.56	3.27	0
1.93	C=C-C-H, O=C-C-H	1.54	0.40	0
1.84	C=C-C-H, HC-C-O, HC-C-N	12.10	3.15	0
1.29	R-CH ₂	0.50	0.13	0

Table S7. Test Results of Acrylic Fiber Spinning Wastewater

Chemical Shift (ppm)	Potential H Type	Percentage (%)	Relative Peak Area	References
>6.0	Ar-H	/	/	0
3.66, 3.61	CH-O	9.73	2.48	0
3.32, 3.28	CH-O	38.09	9.71	0
3.09, 3.07	CH-N	6.16	1.57	00
2.97	CH-N, HC-C-O	4.98	1.27	0
2.74	CH-N, HC-C-O	11.61	2.96	0
2.13	C=C-C-H, O=C-C-H	24.36	6.21	0
1.87	C=C-C-H, HC-C-O, HC-C-N	2.39	0.61	0
1.53	R-CH ₂	2.67	0.68	0

Table S8. Test Results of Acrylic Fiber Mixed Wastewater

Chemical Shift (ppm)	Potential H Type	Percentage (%)	Relative Peak Area	References
>7.0	Ar-H	/	/	0
5.09, 4.97	C=CH	10.70	4.96	00
3.68, 3.64, 3.58	CH-O	17.73	8.22	0
3.41	CH-O	4.55	2.11	0
3.21, 3.16	CH-O	15.85	7.35	0
3.05	CH-N	8.39	3.89	00
2.86, 2.79	CH-N, HC-C-O	11.04	5.12	0
2.68	CH-N, HC-C-O	4.59	2.13	0
2.53	CH-N, HC-C-O	5.87	2.72	0
2.41	CH-N, HC-C-O	2.31	1.07	0
2.10	C=C-C-H, O=C-C-H	4.23	1.96	0
1.87	C=C-C-H, HC-C-O, HC-C-N	13.91	6.45	0
1.29	R-CH ₂	0.82	0.38	0

The top 20 semi-volatile organic compounds and the top 10 volatile organic compounds in acrylonitrile mixed wastewater, acrylic fiber polymerization wastewater, acrylic fiber spinning wastewater, and acrylic fiber mixed wastewater, ranked by peak area in descending order, are presented in Tables S9-S16.

Table S9. Screening Results of C18 Solid-phase Extraction -GC×GC-QTOF for Acrylonitrile Mixed Wastewater (Top 20 Compounds)

Number	Compound Name	CAS	Molecular Formula	Peak Area (Total=222352)	Relative Content (%)
1	2,6,10,14-Tetramethyl-heptadecan	18344-37-1	C ₂₁ H ₄₄	84737	38.1

2	5-Nonanylbenzene	20216-88-0	C ₁₅ H ₂₄	34440	15.5
3	3,5-Dimethyl octane	15869-93-9	C ₁₀ H ₂₂	28634	12.9
4	4,6-Dimethylundecane	8344-37-1	C ₁₃ H ₂₈	22202	10.0
5	Sulfurous acid, butyl tetradecyl ester	959067-52-8	C ₁₈ H ₃₈ O ₃ S	20161	9.1
6	Methoxyacetic acid, 4-tetradecyl ester	361149-16-8	C ₁₇ H ₃₄ O ₃	12022	5.4
7	Sulfurous acid, 2-ethylhexyl nonyl ester	959311-38-7	C ₁₇ H ₃₆ O ₃ S	2557	1.1
8	Methoxyacetic acid, 2-methylpropyl ester	959246-60-7	C ₇ H ₁₄ O ₃	1584	0.7
9	Sulfurous acid, hexyl pentadecyl ester	959039-36-2	C ₂₁ H ₄₄ O ₃ S	1574	0.7
10	Sulfurous acid, butyl tridecyl ester	959067-51-7	C ₁₇ H ₃₆ O ₃ S	1459	0.7
11	3,6,6-Trimethyl-2-Cyclohexen-1-One	23438-77-9	C ₉ H ₁₄ O	1253	0.6
12	2,5,6-Trimethyloctane	62016-14-2	C ₁₁ H ₂₄	1208	0.5
13	Sulfurous acid, 2-propyl tridecyl ester	959312-60-8	C ₁₆ H ₃₄ O ₃ S	1057	0.5
14	Oxalic acid, allyl nonyl ester	959078-60-5	C ₁₄ H ₂₄ O ₄	982	0.4
15	Methyl palmitate	112-39-0	C ₁₇ H ₃₄ O ₂	964	0.4
16	5-Methyl-5-ethyldecan	17312-74-2	C ₁₃ H ₂₈	882	0.4
17	9-Fluorenylmethyl N- (2,5-dioxo-3-pyrrolidinyl) carbamate	323187-10-6	C ₁₉ H ₁₆ N ₂ O ₄	660	0.3
18	Sulfurous acid, hexyl octyl ester	959067-59-5	C ₁₄ H ₃₀ O ₃ S	599	0.3
19	2,7-dimethyl-	1072-16-8	C ₁₀ H ₂₂	595	0.3
20	2-phenylpyrimidine	7431-45-0	C ₁₀ H ₈ N ₂	570	0.3

Table S10. Screening Results of Purge and Capture -GC×GC-QTOF for Acrylonitrile Mixed Wastewater (Top 10 Compounds)

Number	Compound Name	CAS	Molecular Formula	Peak Area (Total=47537)	Relative Content (%)
1	Azabenzene*	110-86-1	C ₅ H ₅ N	8273	17.4

2	Solmethine*	75-09-2	CH ₂ Cl ₂	6981	14.7
3	3-Methylpyridine	108-99-6	C ₆ H ₇ N	4126	8.7
4	6-Isocedrol	19903-73-2	C ₁₅ H ₂₆ O	2589	5.4
5	Albocarbon*	91-20-3	C ₁₀ H ₈	2509	5.3
6	Oxazole	288-42-6	C ₃ H ₃ NO	2487	5.2
7	2-Ethenylpyrazine	4177-16-6	C ₆ H ₆ N ₂	2456	5.2
8	2-Methylnaphthalene*	91-57-6	C ₁₁ H ₁₀	2035	4.3
9	Tetramethylbenzene	527-53-7	C ₁₀ H ₁₄	1784	3.8
10	Pentane, 3-methyl-*	96-14-0	C ₆ H ₁₄	1634	3.4

Note: * indicates compounds that have been verified and detected using standard chemicals.

Table S11. Screening Results of C18 Solid-phase Extraction -GC×GC-QTOF in Acrylic Fiber Polymerization Wastewater (Top 20 Compounds)

Number	Compound Name	CAS	Molecular Formula	Peak Area (Total=158190)	Relative Content (%)
1	2,6,10-Trimethyl-dodecan	3891-98-3	C ₁₅ H ₃₂	70604	44.6
2	4,6-Dimethylundecane	17312-82-2	C ₁₃ H ₂₈	21467	13.6
3	4-Aethyl-octan	15869-86-0	C ₁₀ H ₂₂	11936	7.5
4	2,5,9-Trimethyldecane	62108-22-9	C ₁₃ H ₂₈	11900	7.5
5	3-Methyl-5-propylnonane	31081-18-2	C ₁₃ H ₂₈	10046	6.4
6	2,6,10,14-Tetramethyl-heptadecan	18344-37-1	C ₂₁ H ₄₄	9927	6.3
7	Methoxyacetic acid, 4-tetradecyl ester	361149-16-8	C ₁₇ H ₃₄ O ₃	4561	2.9
8	Sulfurous acid, 2-ethylhexyl nonyl ester	959311-38-7	C ₁₇ H ₃₆ O ₃ S	1842	1.2
9	Sulfurous acid, dodecyl 2-propyl ester	959002-57-4	C ₁₅ H ₃₂ O ₃ S	1807	1.1
10	3,4-dimethylspiro[5.6]dodec-3-en-12-one	478174-73-1	C ₁₄ H ₂₂ O	969	0.6
11	1,3-Diaminopropane	109-76-2	C ₃ H ₁₀ N ₂	890	0.6
12	Methoxyacetic acid, 2-methylpropyl ester	959246-60-7	C ₇ H ₁₄ O ₃	802	0.5
13	3-nonene-1-ol	10339-61-4	C ₉ H ₁₈ O	796	0.5
14	Oxalic acid, allyl decyl ester	959078-61-6	C ₁₅ H ₂₆ O ₄	713	0.5

15	1,1-Diethoxy-2-methoxyethane	4819-75-4	C ₇ H ₁₆ O ₃	568	0.4
16	Cymene	527-84-4	C ₁₀ H ₁₄	491	0.3
17	Oxalic acid, allyl nonyl ester	959078-60-5	C ₁₄ H ₂₄ O ₄	480	0.3
18	N-n-butylhydroxylamine	5080-24-0	C ₄ H ₁₁ NO	476	0.3
19	Oxalic acid, butyl cyclobutyl ester	959002-65-4	C ₁₀ H ₁₆ O ₄	468	0.3
20	2-Ethyl-4-methylpentanol	106-67-2	C ₈ H ₁₈ O	445	0.3

Table S12. Screening Results of Purge and Capture -GC×GC-QTOF for Acrylic Fiber Polymerization Wastewater

Number	Compound Name	CAS	Molecular Formula	Peak Area (Total=5839)	Relative Content (%)
1	1,2-dimethyl 1,2,4-benzenetricarboxylate	54699-35-3	C ₁₁ H ₁₀ O ₆	1404	24.1
2	1-Benzyl-1H-indole	3377-71-7	C ₁₅ H ₁₃ N	1348	23.1
3	Ethyl 4-etoxybenzoate	23676-09-7	C ₁₁ H ₁₄ O ₃	1291	22.1
4	A-Oxoditane*	119-61-9	C ₁₃ H ₁₀ O	788	13.5
5	Sulfurous acid, 2-ethylhexyl isohexyl ester	959067-99-3	C ₁₄ H ₃₀ O ₃ S	519	8.9
6	Sulfurous acid, butyl nonyl ester	959226-13-2	C ₁₃ H ₂₈ O ₃ S	489	8.4

Note: * indicates compounds that have been verified and detected using standard chemicals.

Table S13. Screening Results of C18 Solid-phase Extraction -GC×GC-QTOF in Acrylic Spinning Wastewater (Top 20 Compounds)

Number	Compound Name	CAS	Molecular Formula	Peak Area (Total=216785)	Relative Content (%)
1	2,6,10-Trimethyl-dodecan	3891-98-3	C ₁₅ H ₃₂	50802	23.4
2	4,6-dimethyldodecane	61141-72-8	C ₁₄ H ₃₀	28715	13.2
3	2-methytridecane	1560-96-9	C ₁₄ H ₃₀	28395	13.1
4	5-Nonanylbenzene	20216-88-0	C ₁₅ H ₂₄	25574	11.8
5	2,6,10,14-tetramethyl-heptadecane	18344-37-1	C ₂₁ H ₄₄	22076	10.2
6	3,5-Dimethyl octane	15869-93-9	C ₁₀ H ₂₂	20389	9.4

7	2,6-Dimethylheptadecane	54105-67-8	C ₁₉ H ₄₀	13219	6.1
8	Sulfurous acid, 2-ethylhexyl nonyl ester	959311-38-7	C ₁₇ H ₃₆ O ₃ S	3476	1.6
9	Methyl palmitate	112-39-0	C ₁₇ H ₃₄ O ₂	2636	1.2
10	4-ethyl-octan	15869-86-0	C ₁₀ H ₂₂	2109	1.0
11	Sulfurous acid, 2-ethylhexyl heptadecyl ester	959275-64-0	C ₂₅ H ₅₂ O ₃ S	1858	0.9
12	3,5-Dimethylhex-1-ene	7423-69-0	C ₈ H ₁₆	1599	0.7
13	5-ethyl-1,3-dimethylbenzene	934-74-7	C ₁₀ H ₁₄	1491	0.7
14	2,4-Dimethyldecane	2801-84-5	C ₁₂ H ₂₆	1331	0.6
15	Sulfurous acid, 2-ethylhexyl isohexyl ester	959067-99-3	C ₁₄ H ₃₀ O ₃ S	1189	0.5
16	Sulfurous acid, 2-propyl tridecyl ester	959312-60-8	C ₁₆ H ₃₄ O ₃ S	1179	0.5
17	2-methyl-p-phthalaldehyde	27587-17-3	C ₉ H ₈ O ₂	880	0.4
18	2,4-Dimethylhexane	589-43-5	C ₈ H ₁₈	841	0.4
19	3,6,6-Trimethyl-2-Cyclohexen-1-One	23438-77-9	C ₉ H ₁₄ O	828	0.4
20	2,2,4,6,6-pentamethyl-	13475-82-6	C ₁₂ H ₂₆	730	0.3

Table S14. Screening Results of Purge and Capture -GC×GC-QTOF for Acrylic Spinning Wastewater (Top 10 Compounds)

Number	Compound Name	CAS	Molecular Formula	Peak Area (Total=89581)	Relative Content (%)
1	Acrylonitrile*	107-13-1	C ₃ H ₃ N	46171	51.5
2	Thiacyclopropane	420-12-2	C ₂ H ₄ S	9810	11.0
3	2,4-di-tert-butylphenol	96-76-4	C ₁₄ H ₂₂ O	6605	7.4
4	6-Isocedrol	19903-73-2	C ₁₅ H ₂₆ O	4940	5.5
5	Pentane, 3-methyl-*	96-14-0	C ₆ H ₁₄	2431	2.7
6	Methyl isocyanate	624-83-9	C ₂ H ₃ NO	1941	2.2
7	Oxalic acid bis(isobutyl) ester	2050-61-5	C ₁₀ H ₁₈ O ₄	1755	2.0
8	Cyclopyrrolone	54036-77-0	C ₄ H ₃ NO	1634	1.8
9	1,2,5-trithiacycloheptane	6576-93-8	C ₄ H ₈ S ₃	1543	1.7
10	Albocarbon*	91-20-3	C ₁₀ H ₈	1380	1.5

Note: * indicates compounds that have been verified and detected using standard chemicals.

Table S15. Screening Results of C18 Solid-phase Extraction -GC×GC-QTOF in Acrylic Fiber Mixed Wastewater (Top 20 Compounds)

Number	Compound Name	CAS	Molecular Formula	Peak Area (Total=847941)	Relative Content (%)
1	Tetratetracontane	7098-22-8	C ₄₄ H ₉₀	107118	12.6
2	2,6,10-Trimethyl-dodecan	3891-98-3	C ₁₅ H ₃₂	90892	10.7
3	2-methyl decane	6975-98-0	C ₁₁ H ₂₄	79709	9.4
4	2-methytridecane	1560-96-9	C ₁₄ H ₃₀	73562	8.7
5	2,4-dimethylheptane	2213-23-2	C ₉ H ₂₀	63129	7.4
6	Dodecane,2,6,11-trimethyl	31295-56-4	C ₁₅ H ₃₂	55488	6.5
7	2,7,10-Trimethyldodecane	74645-98-0	C ₁₅ H ₃₂	51531	6.1
8	2,6,10,14-Tetramethyl-heptadecan	18344-37-1	C ₂₁ H ₄₄	43623	5.1
9	2,6-Dimethylheptadecane	54105-67-8	C ₁₉ H ₄₀	38556	4.5
10	1,2,3-Trithiolane	62601-92-7	C ₂ H ₄ S ₃	36149	4.3
11	11-decyl-tetracosane	55429-84-0	C ₃₄ H ₇₀	34660	4.1
12	3,5-Dimethyl octane	15869-93-9	C ₁₀ H ₂₂	33017	3.9
13	Sulfurous acid, butyl hexadecyl ester	959067-54-0	C ₂₀ H ₄₂ O ₃ S	25934	3.1
14	Methoxyacetic acid, 4-tetradecyl ester	361149-16-8	C ₁₇ H ₃₄ O ₃	18065	2.1
15	1,2-Diacetin	102-62-5	C ₇ H ₁₂ O ₅	15537	1.8
16	1,2,5,6-tetrathiacyclooctane	1940-01-8	C ₄ H ₈ S ₄	13866	1.6
17	Methyldodecane	6117-97-1	C ₁₃ H ₂₈	13647	1.6
18	Sulfurous acid, butyl dodecyl ester	959095-65-9	C ₁₆ H ₃₄ O ₃ S	5766	0.7
19	Carbonic acid, eicosyl vinyl ester	2243791-78-6	C ₂₃ H ₄₄ O ₃	3906	0.5
20	Sulfurous acid, hexyl pentadecyl ester	959039-36-2	C ₂₁ H ₄₄ O ₃ S	3370	0.4

Table S16. Screening Results of Purge and Capture -GC×GC-QTOF for Acrylic Fiber Mixed Wastewater (Top 10 Compounds)

Number	Compound Name	CAS	Molecular Formula	Peak Area (Total=4218847)	Relative Content (%)
1	1,2,3-Trithiolane	6669-39-2	C ₂ H ₄ S ₃	60303	27.6
2	Thiacyclopropane	420-12-2	C ₂ H ₄ S	42114	19.2
3	1,2,5-trithiepane	6576-93-8	C ₄ H ₈ S ₃	17751	8.1
4	Pentane, 3-methyl-*	96-14-0	C ₆ H ₁₄	16584	7.6
5	Acrylonitrile*	107-13-1	C ₃ H ₃ N	10840	5.0
6	2,4-di-tert-butylphenol	96-76-4	C ₁₄ H ₂₂ O	6071	2.8
7	Solmethine*	75-09-2	CH ₂ Cl ₂	4104	1.9
8	Miazine	289-95-2	C ₄ H ₄ N ₂	3713	1.7
9	6-Isocedrol	19903-73-2	C ₁₅ H ₂₆ O	3116	1.4
10	4,4'-bi-4H-pyran, 2,2',6,6'-tetrakis (1,1-dimethylethyl) -4,4'-dimethyl-	2557116-35-3	C ₂₈ H ₄₆ O ₂	2968	1.4

Note: * indicates compounds that have been verified and detected using standard chemicals.

This study identified certain compounds that were not initially targeted during screening. The specific compound information is presented in Table S17.

Table S17. Compounds Verified Using Standards

Number	Compound Name	CAS	Molecular Formula
1	Azabenzene	110-86-1	C ₅ H ₅ N
2	Solmethine	75-09-2	CH ₂ Cl ₂
3	Albocarbon	91-20-3	C ₁₀ H ₈
4	2-Methylnaphthalene	91-57-6	C ₁₁ H ₁₀
5	A-Oxoditane	119-61-9	C ₁₃ H ₁₀ O
6	Acrylonitrile*	107-13-1	C ₃ H ₃ N
7	Pentane, 3-methyl-	96-14-0	C ₆ H ₁₄

The compounds in acrylic fiber polymerization wastewater and acrylic fiber mixed wastewater were classified according to ionization modes (negative: −; positive: +) and retention time. The results are presented in Tables S18 and S19, respectively.

Table S18. Screening results of compounds for acrylic fiber polymerization wastewater using UPLC-Q-Orbitrap

Retention Time (min)	Compound name	Molecular formula	Compound category	Relative content (%)
1.88±0.72 (−)	Piperazine-1-carboxylic acid, 4- (5-methoxy-2,4-dimethylbenzenesulfonyl) -, ethyl ester	C ₁₆ H ₂₄ N ₂ O ₅ S	Esters	57.39
3.40±0.79 (−)	3H-1,2-Dithiolo[3,4-b]pyridin-3-one	C ₆ H ₃ NOS ₂	Nitrogen-containing heterocyclic compounds	23.08
4.53±0.33 (−)	2-propenoic acid, 2-methyl-, 4- (phenylamino) sulfonylphenyl ester	C ₁₆ H ₁₅ NO ₄ S	Esters	2.85
1.36±0.21 (+)	all-trans-OH-Spirilloxanthin	C ₄₁ H ₅₈ O ₂	Ethers	4.38
2.07±0.49 (+)	/	C ₂₅ H ₃₇ NO ₂	Ketones	5.74
2.94±0.37 (+)	Reserpine	C ₃₃ H ₄₀ N ₂ O ₉	Esters	6.55

Note: The compounds in the table are arranged according to the negative ion mode (−), positive ion mode (+), and retention time

Table S19. Screening results of compounds for acrylic fiber mixed wastewater using UPLC-Q-Orbitrap

Retention Time (min)	Compound name	Molecular formula	Compound category	Relative content (%)
1.80±0.64 (−)	2-Ethyl-4,6-Dimethylpyridine	C ₉ H ₁₃ N	Nitrogen-containing heterocyclic compounds	43.11

3.18±0.64 (-)	4,4'-Dihydroxy-2-Methoxy-3-prenylchalcone	C ₂₁ H ₂₂ O ₄	Ketones	34.07
4.45±0.24 (-)	Acetazolamide tri-methyl derivative	C ₇ H ₁₂ N ₄ O ₃ S ₂	Acid amides	1.47
5.11±0.41 (-)	3-Isopropyl-5,5-dimethyl-1,2,3,4a,5,6,7,8,9,9a decahydro-4-oxa-3-azafluorene-2-carbonitrile	C ₁₇ H ₂₆ N ₂ O	Nitriles	1.04
6.45±0.19 (-)	Sydonol, dimethyl ether	C ₁₇ H ₂₈ O ₃	Ethers	0.35
7.45±0.80 (-)	5H-[1,2,4]Triazolo[3,4-b][1,3]thiazin-5-one, 7- (4-methoxyphenyl) -3-propyl-	C ₁₅ H ₁₅ N ₃ O 2S	Acid amides	1.81
1.86±0.71 (+)	Astaxanthin	C ₄₀ H ₅₂ O ₄	Ketones	10.41
4.01±0.71 (+)	Sebacic acid, propyl tridec-2-ynyl ester	C ₂₆ H ₄₆ O ₄	Esters	7.75

Note: The compounds in the table are arranged according to the negative ion mode (-), positive ion mode (+), and retention time

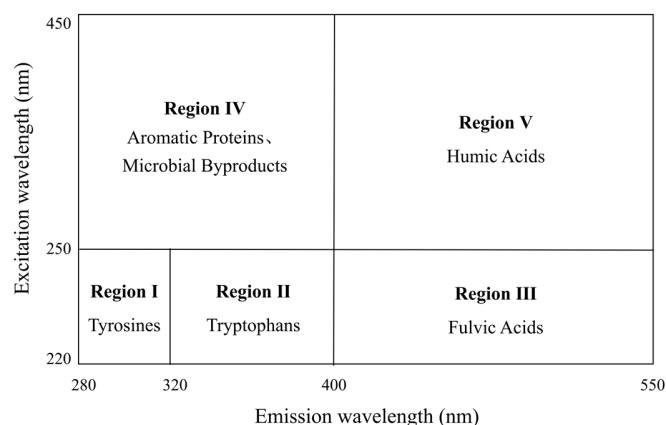


Figure S2. Three-dimensional fluorescence spectral partitioning of DOM

After pretreatment of the acrylic fiber mixed wastewater sample using C18 and HLB solid-phase extraction followed by vacuum freeze-drying, the two-dimensional chromatogram obtained from the GC×GC-QTOF analysis is presented in Figure S3.

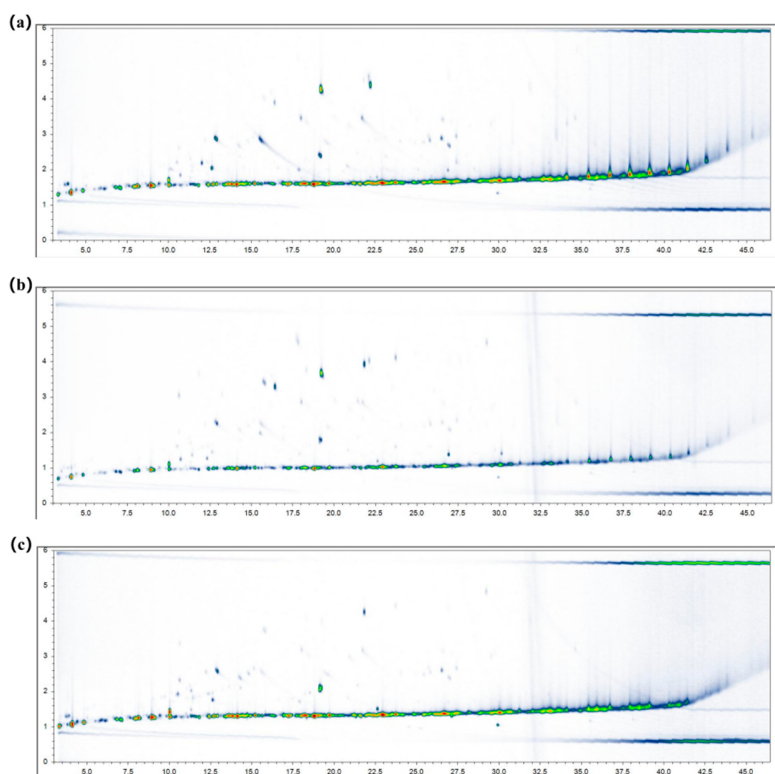


Figure S3. Two-dimensional chromatogram of the acrylic fiber mixed wastewater (a) C18 solid-phase extraction (b) HLB solid-phase extraction and (c) Vacuum freeze-drying methods

Note: The horizontal and vertical axes correspond to the one-dimensional retention time (in minutes) and the two-dimensional retention time (in seconds) of the unknown compound on the chromatographic column, respectively.

The three-dimensional excitation-emission matrices (EEMs) and corresponding two-dimensional chromatograms of acrylonitrile mixed wastewater, acrylic fiber polymerization wastewater, acrylic fiber spinning wastewater, and acrylic fiber mixed wastewater samples, following C18 solid-phase extraction pretreatment, are presented in Figures S4 and S5.

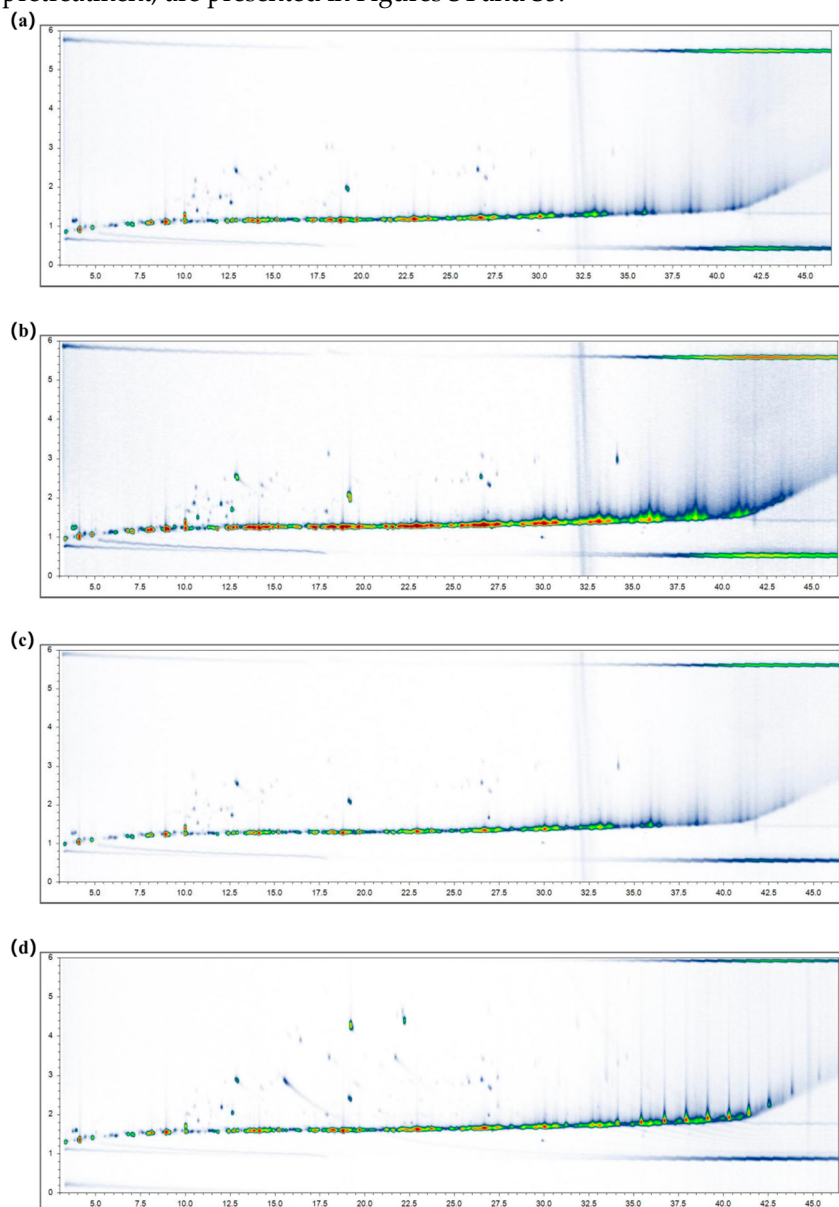


Figure S4. Two-dimensional chromatograms of samples from different wastewater (a) Acrylonitrile mixed wastewater (b) Acrylic fiber polymerization wastewater (c) Acrylic fiber spinning wastewater and (d) Acrylic fiber mixed wastewater after pretreatment by C18 solid-phase extraction method

Note: The horizontal and vertical axes correspond to the one-dimensional retention time (in minutes) and the two-dimensional retention time (in seconds) of the unknown compound on the

chromatographic column, respectively.

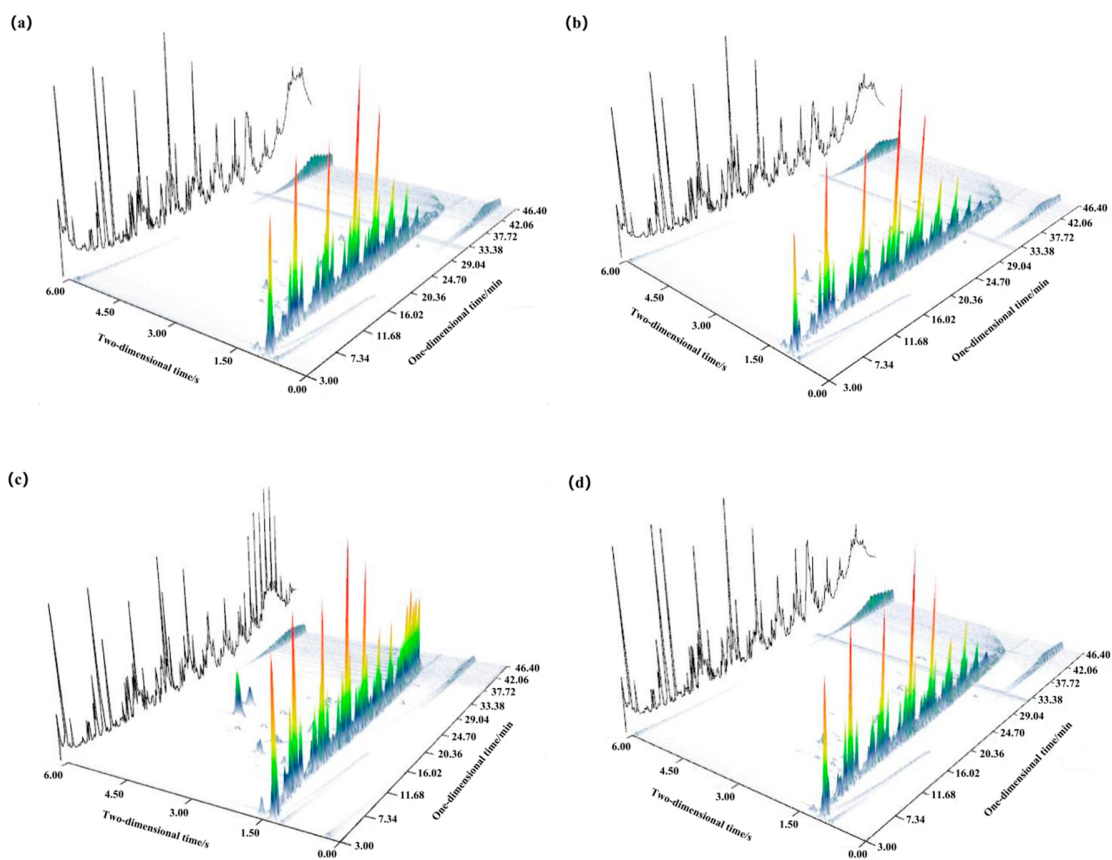


Figure S5. Three-dimensional chromatographic views of samples from different wastewater (a) Acrylonitrile mixed wastewater (b) Acrylic fiber polymerization wastewater (c) Acrylic fiber spinning wastewater and (d) Acrylic fiber mixed wastewater after pretreatment by C18 solid-phase extraction method

The three-dimensional views and two-dimensional chromatograms of the samples of acrylonitrile mixed wastewater, acrylic fiber polymerization wastewater, acrylic fiber spinning wastewater and acrylic fiber mixed wastewater after treatment by purge and trap method are shown in Figures S6 and S7.

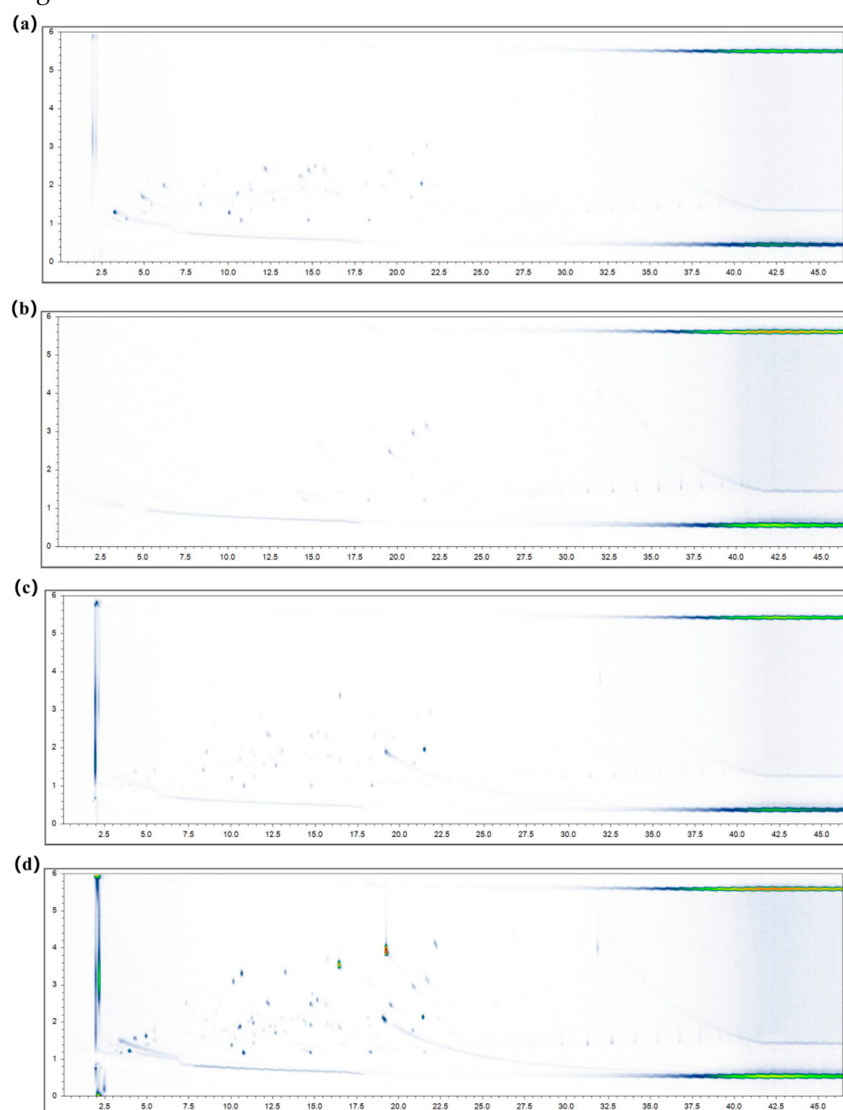


Figure S6. Two-dimensional chromatograms of (a) Acrylonitrile mixed wastewater (b) Acrylic fiber polymerization wastewater (c) Acrylic fiber spinning wastewater and (d) Acrylic fiber mixed wastewater after pretreatment by purge and trap method

Note: The horizontal and vertical axes correspond to the one-dimensional retention time (in minutes) and the two-dimensional retention time (in seconds) of the unknown compound on the chromatographic column, respectively.

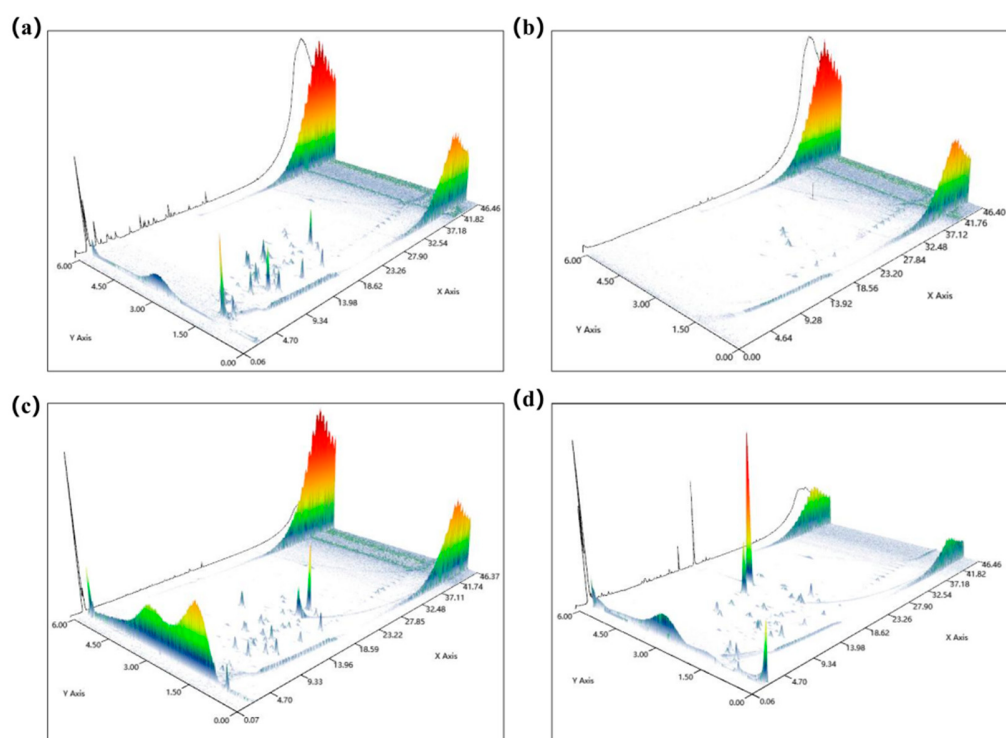


Figure S7. Three-dimensional chromatographic views of (a) Acrylonitrile mixed wastewater (b) Acrylic fiber polymerization wastewater (c) Acrylic fiber spinning wastewater and (d) Acrylic fiber mixed wastewater after pretreatment by purge and trap method

After pretreatment of the acrylic fiber mixed wastewater samples via C18 and HLB solid-phase extraction combined with vacuum freeze-drying, the total ion chromatogram (TIC) obtained by UPLC-Q-Orbitrap analysis is shown in Figure S8.

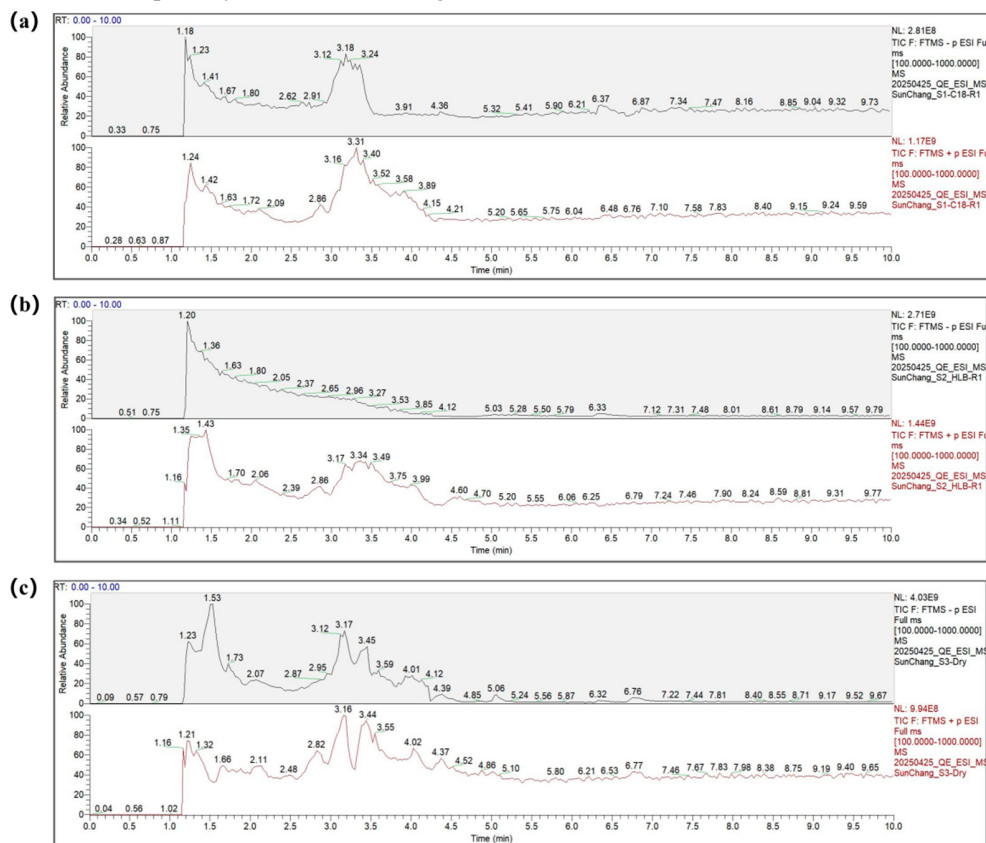


Figure S8. Total ion chromatogram of the pre-treated acrylic fiber mixed wastewater with different pretreatments (a)C18 solid-phase extraction (b)HLB solid-phase extraction (c) vacuum freeze-drying

The total ion chromatograms of acrylonitrile mixed wastewater, acrylic fiber polymerization wastewater, acrylic fiber spinning wastewater and acrylic fiber mixed wastewater samples obtained by UPLC-Q-Orbitrap testing are shown in Figure S9.

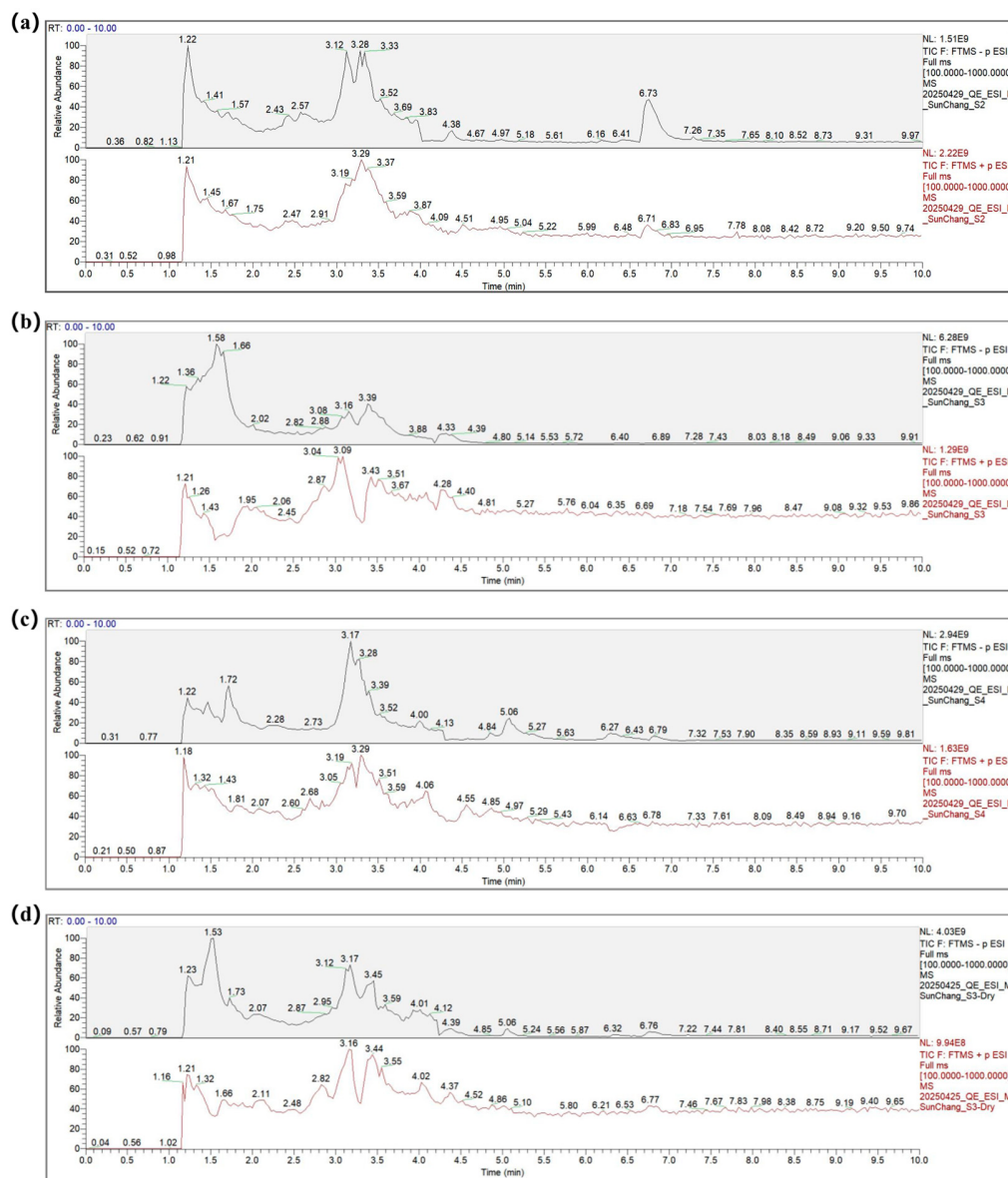


Figure S9. Total ion chromatogram of samples from different wastewater (a) Acrylonitrile mixed wastewater (b) Acrylic fiber polymerization wastewater (c) acrylic fiber spinning wastewater (d) Acrylic fiber mixed wastewater

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