RayKol

Knowledge Optimized Laboratory

Detection of Perfluorinated Compounds in Drinking Water Sample Pre-treatment Solution

A Comprehensive Business Group of Smart Laboratory and Big Health Field

Background Introduction

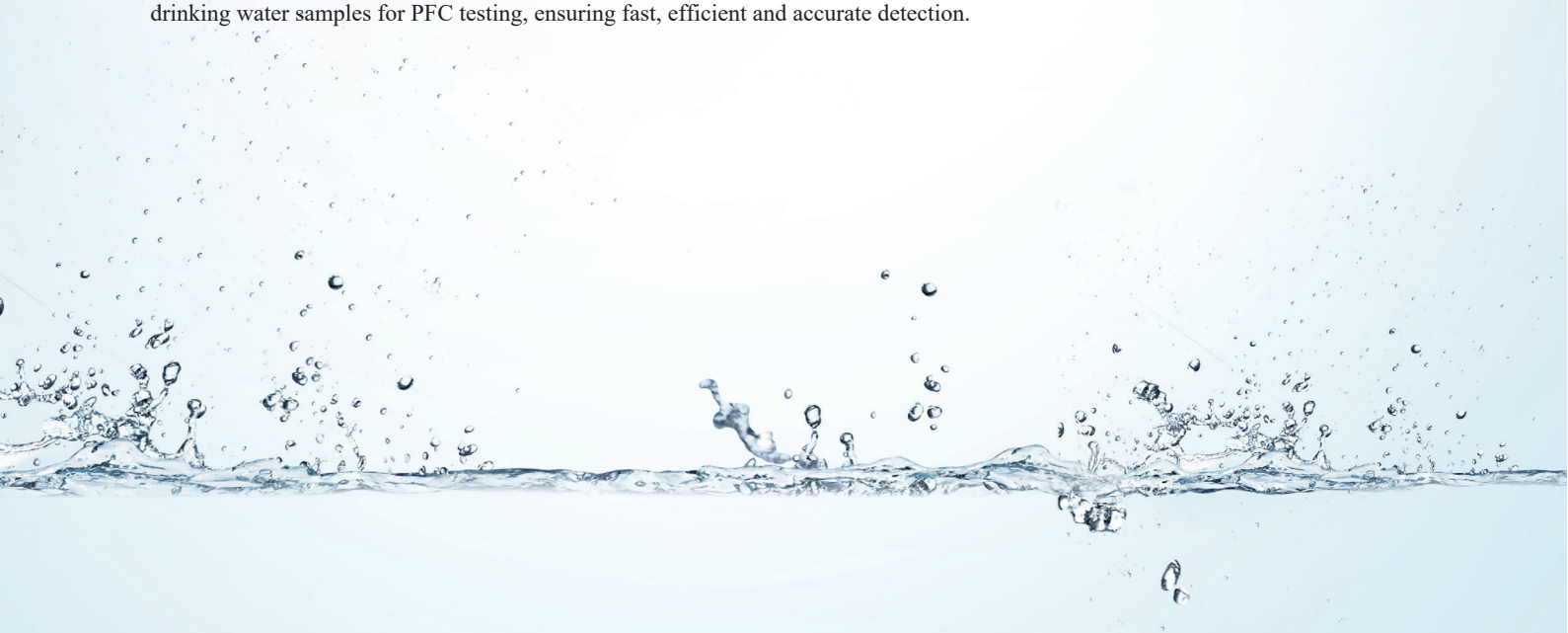
Since their production began in the 1950s, perfluorinated compounds (PFCs), serving as surfactants and protective agents, have been widely used in industrial manufacturing and everyday items, such as carpets, leather, floor wax, etc. PFCs are characterized by their high toxicity, persistence, bioaccumulation, and the ability to migrate over long distances, similar to persistent organic pollutants. In 2009, the Stockholm Convention classified perfluorooctane sulfonic acid (PFOS) and its salts as persistent organic pollutants. On June 2 of this year, the Chinese Ministry of Ecology and Environment emphasized at its regular press conference in May that persistent organic pollutants would be included in the national environmental monitoring system. The recently released Outline of Ecological Environment Monitoring Planning (2020-2035) by Ministry of Ecology and Environment also highlighted the importance of enhancing the monitoring capabilities and levels for persistent organic pollutants.

PFCs in domestic wastewater are discharged into the environment through sewage treatment plants and enter the environment and organisms through water, soil, air and other media. Since drinking water is one of the main routes through which the population is exposed to PFCs, simultaneous determination of various PFCs, especially short-chain (carbon number < 8) and medium-long chain (8 ≤ carbon number ≤ 10) PFCs in drinking water is very necessary for ensuring the safety of drinking water.

Methods for Detecting Perfluorinated Compounds	Gas Chromatography-Mass Spectrometry Capillary Electrophoresis Liquid Chromatography-Mass Spectrometry Ultra-Performance Liquid Chromatography Tandem Mass Spectrometry
Main Pre-treatment Methods for Perfluorinated Compounds	Solid Phase Extraction

Solid Phase Extraction has the advantages of simple operation, low solvent consumption, fewer analytical steps and time, and a wide range of applicability.

Raykol offers automated sample pre-treatment solutions for the analysis of PFCs in drinking water. By incorporating automated pre-treatment equipment into the entire testing process, Raykol assists laboratory personnel in rapidly and pollution-freely pre-treating drinking water samples for PFC testing, ensuring fast, efficient and accurate detection.



Equipment, Reagents and Consumables

Equipment	Reagents	Consumable
RayKol Fotector Plus Automated Solid Phase Extraction	Methanol, Ammonium Acetate (HPLC-MS grade)	0.22 μm Acetate Cellulose Filter Membrane
Raykol Auto EVA 80 Fully Automatic Parallel Concentrator		
Waters ACQUITY UPLC-XEVO Micro TQS Ultra High Pressure Liquid Chromatography - Tandem Mass Spectrometer	Ammonia Water (HPLC-MS grade)	Oasis WAX Solid Phase Extraction Column (150 mg, 6 mL)
Ultrasonic Cleaning Machine		
Vortex Oscillator	Ammonium Acetate, Glacial Acetic Acid (Analytical grade)	Acquity UPLC™ BEH C18 Chromatography Column (1.7 μm, 2.1 mm × 50 mm)
Electronic Balance (sensitivity 0.0001 g)		

Standard Substance:

Perfluorobutanoic Acid (PFBA), Perfluoropentanoic Acid (PFPA), Perfluorohexanoic Acid (PFHxA), Perfluoroheptanoic Acid (PFHpA), Perfluorooctanoic Acid (PFOA), Perfluorononanoic Acid (PFNA), Perfluorodecanoic Acid (PFDA), Perfluorobutanesulfonic Acid (PFBS), Perfluorohexanesulfonic Acid (PFHxS), Perfluoroheptanesulfonic Acid (PFHpS), Perfluorooctanesulfonic Acid (PFOS), 13C2-Perfluorohexanoic Acid (MPFHxA), 13C4-Perfluorooctanoic Acid (MPFOA), 13C4-Perfluorooctanesulfonic Acid (MPFOS).

Pre-treatment Main Instrument Introduction

Fotector series Automated Solid Phase Extraction

Targeted material selection

For the design of the PFC project in water, all contact materials are made of PEEK material, ensuring an effectively controllable background.

Simultaneous processing of multiple samples

The instrument automatically completes the entire solid-phase extraction process through six channels: column activation, sample loading, washing, drying, elution, and stepwise collection;

Large-scale sample continuous purification

Enables the continuous enrichment and purification of at least 60 samples;

Wide compatibility

Compatible with solid-phase extraction columns of various sizes, including 1mL, 3mL, 6mL, etc., applicable to pre-treatment of different water quality samples and other environmental samples.

Auto EVA 80 Automated Evaporation System

Multi-channel controllable design tailored to customer needs

Allows individual control of airflow in each channel; features a quick-detachable design for nitrogen blowing needles, facilitating easy cleaning and use, significantly improving the operational experience of laboratory personnel;

Patented variable diameter nitrogen blowing needles for excellent parallelism in nitrogen blowing

Utilizes high-strength variable diameter nitrogen blowing needles, positioning the tip of the needle in the middle of the sample tube; each needle tip has the same inner diameter, ensuring consistent flow rate across all tips, providing uniformity for sample concentration;

Transparent water bath heating box for unobstructed observation

Designed with three transparent glass sides, greatly enhancing the visibility of the sample rack area, allowing laboratory personnel to easily observe the nitrogen blowing concentration process.

Pre-treatment Process

Water sample processing	For a 1L water sample, add 100μL of 100μg/L internal standard and mix well. add ammonium acetate to adjust the pH to 6.8-7.0.
Activate the column	Use 5mL of 0.1% ammonia-methanol solution for activation, followed by 7mL of methanol and 10mL of ultrapure water.
Load the sample	Load the water sample at a flow rate of 8mL/min.
Wash	Wash with 5mL of 25mmol/L ammonium acetate solution (pH=4) and 12mL of ultrapure water.
Dry	Dry the small column for 15 minutes.
Elute	Elute with 5mL of methanol and 7mL of 0.1% ammonia-methanol solution.
Concentrate	Nitrogen blow to near dryness (water bath temperature ≤40°C).
Volumetric preparation for analysis	Reconstitute with a 30% methanol solution (3:7, V/V), dilute to 1mL, vortex mix well, then proceed to instrumental analysis.

Fotector series
Automated Solid Phase Extraction

Auto EVA 80
Automated Evaporation System

Instrument Blank Inspection

To verify whether the Fotector Plus high-throughput fully automatic solid-phase extraction instrument introduces any target analyte residues or contaminants during the sample pretreatment process, two pure water blank samples were processed using the pretreatment method before starting the instrument and after the experiment ended. The results were determined by ultra-high performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). The results showed that the target analytes were not detected in the blank samples processed at startup and in the blank samples processed after the actual samples, indicating that the instrument does not leave residues in the samples during processing and does not introduce contaminants.

The detection results are shown in the following table:

Target Compound	Start-up Blank		End-of-experiment Blank		Method Detection Limit (ng/L)
	Measured value1 (ng/L)	Measured value2 (ng/L)	Measured value1 (ng/L)	Measured value2 (ng/L)	
Perfluorobutanoic Acid	ND	ND	ND	ND	3.0
Perfluoropentanoic Acid	ND	ND	ND	ND	3.0
Perfluorohexanoic Acid	ND	ND	ND	ND	1.5
Perfluoroheptanoic Acid	ND	ND	ND	ND	0.5
Perfluorooctanoic Acid	ND	ND	ND	ND	1.5
Perfluorononanoic Acid	ND	ND	ND	ND	0.5
Perfluorodecanoic Acid	ND	ND	ND	ND	2.0
Perfluorobutanesulfonic Acid	ND	ND	ND	ND	2.0
Perfluorohexanesulfonic Acid	ND	ND	ND	ND	2.0
Perfluoroheptanesulfonic Acid	ND	ND	ND	ND	2.0
Perfluorooctanesulfonic Acid	ND	ND	ND	ND	2.0

Experimental Conclusion

This scheme has established a solid-phase extraction-ultra-high performance liquid chromatography-tandem mass spectrometry method for the analysis of 11 perfluorinated compounds in drinking water. This method features a wide linear range, low detection and quantification limits, and its accuracy and precision are suitable for the simultaneous determination of various perfluorinated compounds in drinking water.

The pre-treatment purification process utilizes the Raykol Fotector Plus fully automatic solid-phase extraction instrument with a precise injection pump to control the volumes for activation and elution, ensuring stable and controllable flow rates for activation, elution, and sample loading. In conjunction, the Raykol Auto EVA 80 high-throughput fully automatic parallel concentrator is used for concentration. The sample racks of both instruments are compatible for use, making operations coherent and straightforward. The detection results have shown excellent recovery rates and RSD outcomes, and the blank determination confirmed that the pre-treatment process did not cause cross-contamination due to residual analysis targets in the instruments, thereby demonstrating that both pre-treatment instruments are suitable for the pre-treatment of perfluorinated compounds detection in drinking water.

Detection Conditions

Ultra-High Performance Liquid Chromatography Conditions

BEH C18 column, column temperature 40°C, injection volume 10 μL, mobile phase A is methanol, mobile phase B is a 5 mmol/L aqueous solution of ammonium acetate, flow rate 0.3 mL/min, gradient elution program as per the table on the right.

Time/min	Mobile Phase A/%	Mobile Phase B/%
0.0	25	75
0.5	25	75
10.0	85	15
10.5	95	5
14.0	95	5
14.1	25	75
16.0	25	75

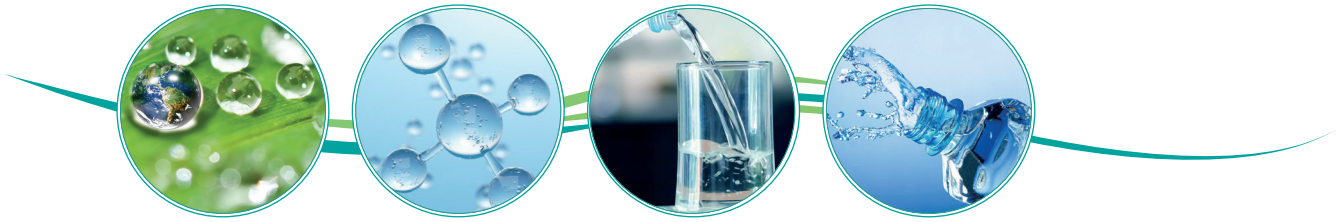
Mass Spectrometry Conditions

Ion source: Electrospray Ionization (ESI), negative ion scan, Multi-Reaction Monitoring (MRM) mode analysis. Source temperature: 150°C, desolvation temperature: 500°C, desolvation gas flow: 1000 L/h, collision gas flow: 50 L/h, capillary voltage: 2.0 kV. High-purity nitrogen is used for desolvation and nebulization, and the collision gas is argon.

Recovery Rate and Relative Standard Deviation of 11 PFCs in Water

Tap water samples were collected and spiked with three concentration levels (low: 5.00 ng/L, medium: 10.00 ng/L, high: 50.00 ng/L) of the 11 PFC standard substances. Six replicates were prepared for each concentration level. The recovery rates and relative standard deviations of the 11 PFCs at different concentration levels were calculated. The recovery rates of the 11 target compounds at the three concentration levels ranged from 90.0-122.0%, 87.1-130.0%, and 80.0-114.0%, with relative standard deviations of 2.0-8.6%, 1.3-9.1%, and 2.2-11.0%, respectively.

Target Compound	Background Concentration (ng/L)	Spiked Concentration (ng/L)	Mean (ng/L)	Standard Deviation	RSD (%)	Average Spiked Recovery Rate (%)
Perfluorobutanoic Acid	4.03	5.00	8.53	0.293	3.4	90.0
	4.03	10.00	13.30	0.169	1.3	92.3
	4.03	50.00	44.00	2.199	5.0	80.0
Perfluoropentanoic Acid	ND	5.00	5.36	0.242	4.5	107.0
	ND	10.00	9.54	0.488	5.1	95.4
	ND	50.00	52.50	1.800	3.4	105.0
Perfluorohexanoic Acid	1.50	5.00	6.46	0.126	2.0	99.1
	1.50	10.00	11.80	0.404	3.4	103.0
	1.50	50.00	48.10	1.041	2.2	93.1
Perfluoroheptanoic Acid	1.26	5.00	6.35	0.201	3.2	102.0
	1.26	10.00	11.70	0.531	4.5	105.0
	2.01	50.00	56.70	2.290	4.1	109.0
Perfluorooctanoic Acid	3.64	5.00	8.23	0.410	5.0	91.9
	3.64	10.00	12.90	0.675	5.2	92.6
	3.64	50.00	57.20	4.270	7.5	107.0
Perfluorononanoic Acid	1.86	5.00	7.30	0.232	3.2	109.0
	0.91	10.00	9.62	0.391	4.1	87.1
	1.86	50.00	49.90	2.540	5.1	96.0
Perfluorodecanoic Acid	ND	5.00	5.50	0.473	8.6	110.0
	ND	10.00	12.10	0.585	4.8	121.0
	ND	50.00	51.60	1.420	2.8	103.0
Perfluorobutanesulfonic Acid	ND	5.00	6.12	0.185	3.0	122.0
	ND	10.00	12.10	0.302	2.5	121.0
	ND	50.00	56.90	5.210	9.2	114.0
Perfluorohexanesulfonic Acid	ND	5.00	6.07	0.186	3.1	121.0
	ND	10.00	10.90	0.251	2.3	109.0
	ND	50.00	51.90	3.930	7.6	104.0
Perfluoroheptanesulfonic Acid	ND	5.00	6.04	0.449	7.4	121.0
	ND	10.00	13.00	1.180	9.1	130.0
	ND	50.00	56.20	5.900	11	112.0
Perfluorooctanesulfonic Acid	ND	5.00	5.66	0.202	3.6	113.0
	ND	10.00	11.30	0.818	7.3	113.0
	ND	50.00	55.10	2.800	5.1	110.0



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