Application Note
Environmental

Comprehensive and Robust Analysis of Ultrashort- to Long-Chain PFAS, PAE, OPE, and PAH

In $PM_{2.5}$ samples using the Plasmion SICRIT and Agilent Revident LC/Q-TOF

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Abstract

Per- and polyfluoroalkyl substances (PFAS), phthalate esters (PAE), organophosphates (OPE), and polycyclic aromatic hydrocarbons (PAH) are atmospheric contaminants commonly found in fine particulate matter ($PM_{2.5}$). These widespread contaminants threaten ecosystems and human health through persistence, bioaccumulation, and toxicity. Escalating environmental and regulatory focus on ultrashort- and short-chain PFAS as persistent and ubiquitous atmospheric contaminants highlight the critical demand for versatile, high-performance analytical instrumentation capable of comprehensive coverage. Conventional liquid chromatography-electrospray ionization-mass spectrometry (LC-ESI-MS) systems perform reliably for medium- to long-chain PFAS but face significant limitations capturing ultrashort-chains in a single analysis, impeding full PFAS characterization of the sample. This application note showcases the capabilities of Plasmion Soft Ionization by Chemical Reaction In Transfer (SICRIT) Technology directly interfaced with the Agilent Revident LC/Q-TOF for analyzing C_2–C_8 PFAS in seasonal atmospheric samples. Coupled with solvent-free solid-phase microextraction (SPME), the dielectric barrier discharge ionization (DBDI) high-resolution tandem mass spectrometry (HRMS/MS) workflow drastically simplifies sample preparation, eliminates solvent consumption, and reduces operational costs.[1] This innovative, ambient-pressure ionization platform delivers efficient ionization from polar ultrashort-chain to less polar long-chain PFAS with high sensitivity of 0.06 to 2.02 pg/m^3, while reducing in-source fragmentation (ISF) versus traditional methods. It is highly practical for routine high-throughput environmental monitoring of multiclasses of contaminants in $PM_{2.5}$.

Introduction

The escalating global production and use of synthetic organic chemicals have resulted in widespread environmental contamination, posing complex risks to the environment and human health. Among the most scrutinized classes of contaminants are PFAS, PAE, OPE, and PAH. These compounds share characteristics of persistence and mobility, yet there may also be potential synergistic toxicity. Their ubiquitous detection in the air makes it essential to understand the four contaminant classes collectively as a whole.

PAE function primarily as plasticizers that impart flexibility to polymers, while OPE have emerged as replacements for phased-out brominated flame retardants. They are both well-known endocrine-disrupting chemicals. PAH are formed during the incomplete combustion of organic matter, such as vehicle exhaust, coal burning, and petroleum refining. Apart from these legacy persistent organic pollutants (POPs) and contaminants, the emerging environmental presence of PFAS presents growing threats. Recent findings highlight that accumulation of ultrashort-chain PFAS, especially the two-carbon trifluoroacetic acid (TFA), has been significantly underestimated. It is used as the substitution for phased-out long-chain counterparts and is formed during atmospheric transformations from long-chain perfluorocarboxylic acids (PFCA) and neutral PFAS precursors.[2]

Comprehensive analysis of PFAS spanning ultrashort- to long-chain species remains challenging because of their wide range of volatility and polarity. Traditional approaches like gas chromatography/mass spectrometry (GC/MS) suit TFA but require derivatization, limiting sensitivity and excluding longer-chain PFAS. While LC-ESI-MS/MS excels at trace-level detection of medium- to long-chain PFAS, it demands separate columns, gradients, and methods for ultrashort-chain analogs, complicating analysis workflows. ESI also suffers from ISF, which reduces selectivity and sensitivity. PFAS contamination is inevitably found in solvents and consumables, hindering trace quantification.

The combination of SICRIT® ionization technology with the Agilent Revident LC/Q-TOF system addresses these challenges head-on, delivering a powerful, streamlined solution for broad-spectrum PFAS profiling and quantification. SICRIT® provides exceptional ionization efficiency across diverse polarities through its soft dielectric barrier discharge process, enabling sensitive detection of volatile ultrashort-chain species alongside less volatile longer-chain PFAS, while substantially reducing ISF for improved sensitivity. Paired with the Revident LC/Q-TOF, this set up leverages high-resolution capabilities for targeted quantification. This is achieved through an extended dynamic range, enhanced acquisition speeds, and doubled (MS/MS) sensitivity. Unlike its predecessors, the Revident LC/Q-TOF features a temperature-controlled flight tube, offering superior stable mass accuracy over extended periods. Unlike traditional data-independent acquisition (DIA), the new Parallel Reaction Monitoring (PRM) acquisition workflow allows unambiguous identification of the targeted analyte by quadrupole isolation of the precursor ion for fragmentation with optimized collision energy. It effectively minimizes the interference from the complex matrix, as well as avoids overlap of coeluting ions with similar retention times and similar fragments.

Experimental

Materials

PAE, OPE, PAH standards, and SPME fibers were purchased from Sigma-Aldrich (St. Louis, MO, USA). PFAS standards were obtained from Alta Scientific (Tianjin, China). From December 2023 to August 2024, 24 $PM_{2.5}$ samples were collected at Zhengzhou University in China.

Instrumentation

A schematic illustration and photo of the instrument set up is shown in Figure 1. Analytes were desorbed for two minutes from SPME fibers using a custom-built SPME holder integrated with a GC/SPME module and a glass inlet liner (Plasmion GmbH, Augsburg, Germany). The optimized SPME parameters are summarized in Table 1. After sample desorption, soft ionization was done by SICRIT® ion source technology (Plasmion GmbH, Augsburg, Germany) operated at 1.6 kV and 15 kHz. Data were collected using an Agilent Revident LC/Q-TOF. The optimized MS instrument parameters are displayed in Table 2. Structural information of the target compounds and their PRM acquisition parameters can be found in Figure 2 and Table 3, respectively. Reference mass calibration was performed using characteristic background ions produced by DBDI, achieving a mass detection accuracy of < 5 ppm.

Table 1. Optimized SPME parameters for PFAS and PAE/OPE/PAH analysis.

	PFAS	PAEs/OPEs/PAHs
SPME Fiber	85 µm polyacrylate	65 µm divinylbenzene/ polydimethylsiloxane
Extraction Temperature	60 °C	100 °C
Extraction Duration	40 min	40 min
Desorption Temperature	240 °C	230 °C

Table 2. Optimized MS parameters for positive and negative ionization modes.

Parameter	Positive	Negative
Gas Temperature	325 °C	200 °C
Gas Flow	8 L/min	8 L/min
Nebulizer	6 psi	6 psi
Capillary Voltage	10 V	10 V
Reference Mass	*m/z* 149.0233 ($[C_8H_5O_3]^+$) and 279.159091 ($[C_{16}H_{23}O_4]^+$)	*m/z* 61.9884 ($[NO_3]^-$) and 124.9840 ($[HNO_3NO_3]^-$)
MS and PRM Acquisition Range	*m/z* 65–1,000	*m/z* 65–1,000
MS and PRM Acquisition Rate	3 and 6 spectra/s	3 and 6 spectra/s
PRM Isolation Width	Narrow (*m/z* 1.3)	Narrow (*m/z* 1.3)

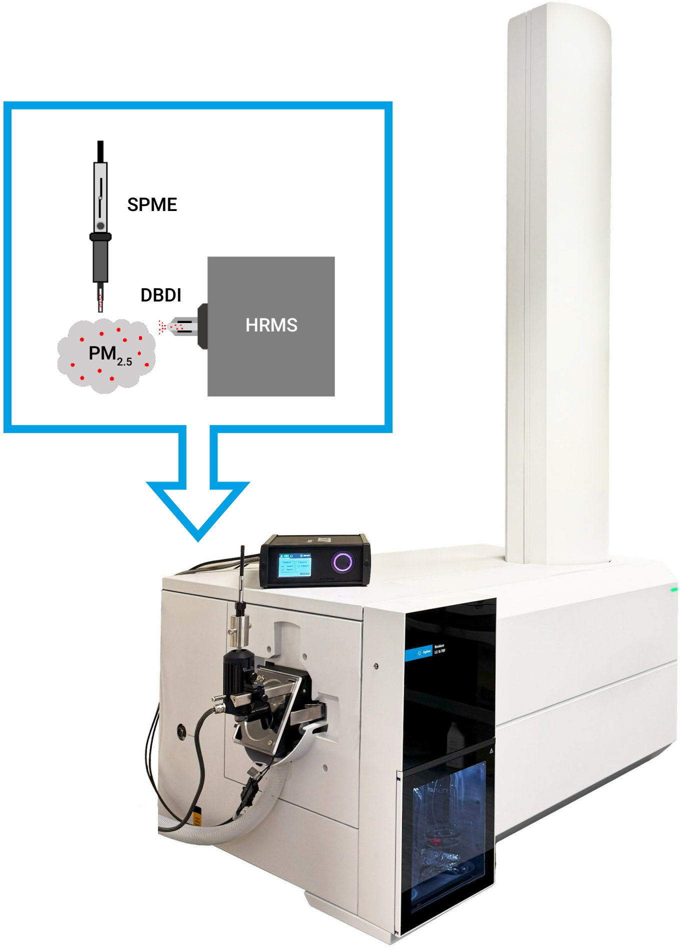

Figure 1. Schematic illustration and photo of the instrument setup. The Plasmion SICRIT ion source is connected to the Agilent Revident LC/Q-TOF, while the controller of SICRIT is placed on top of it.

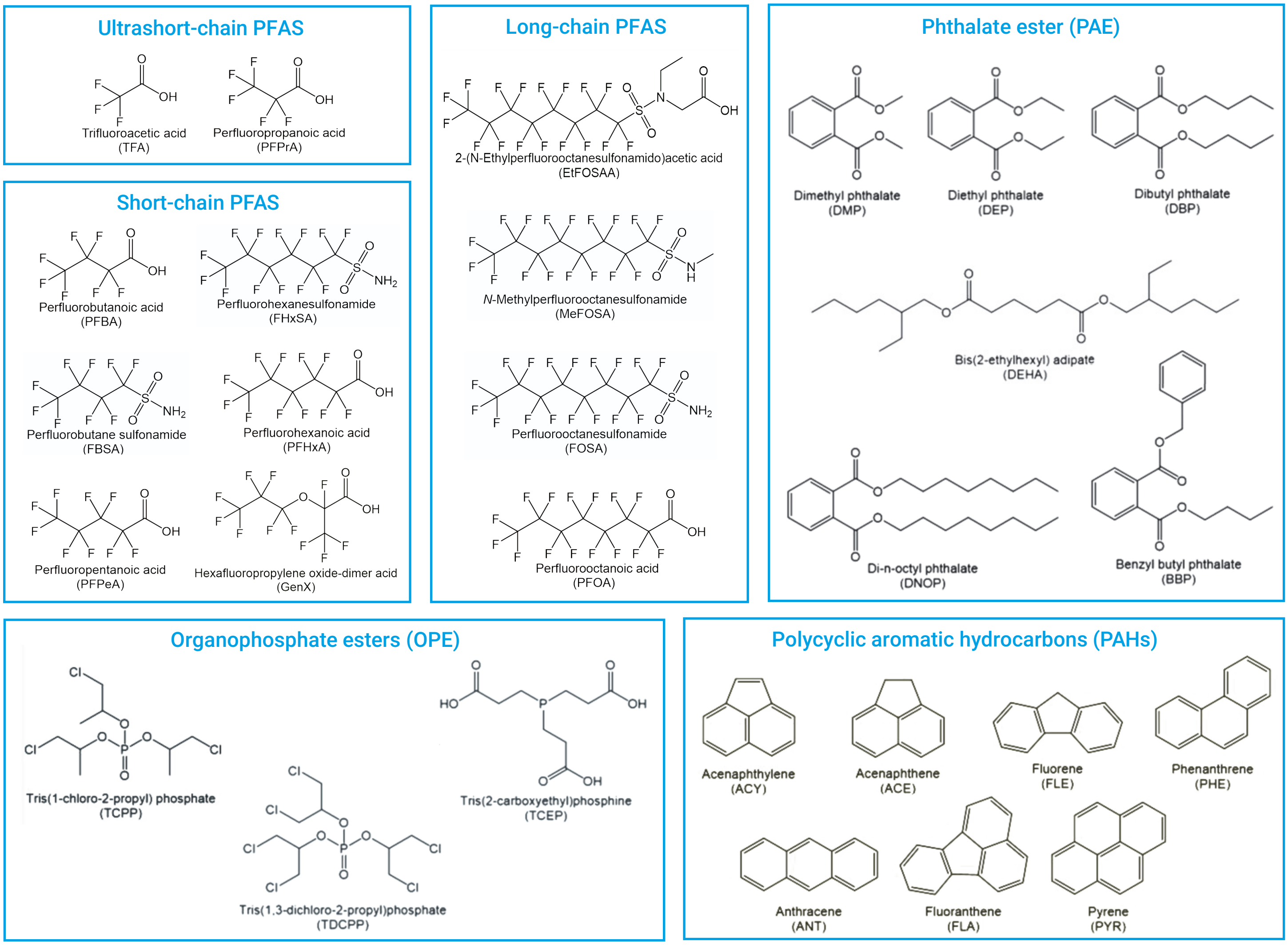

Figure 2. Structural information and classification of the targeted PFAS, PAEs, OPEs, and PAHs.

Table 3. Target compounds and PRM acquisition parameters.

Compound Class	Compound Name	Compound Formula	Polarity	Precursor Ion Species	PRM Transition	Fragmentor (V)	CE (V)
PFAS	TFA	$C_2HF_3O_2$	Negative	$[M-H]^-$	113 → 69	100	10
PFAS	PFPrA	$C_3HF_5O_2$	Negative	$[M-H]^-$	163 → 119	100	10
PFAS	PFBA	$C_4HF_7O_2$	Negative	$[M-H]^-$	213 → 169	100	5
PFAS	PFPeA	$C_5HF_9O_2$	Negative	$[M-H]^-$	263 → 219	100	5
PFAS	PFHxA	$C_6HF_{11}O_2$	Negative	$[M-H]^-$	313 → 269	100	5
PFAS	PFOA	$C_8HF_{15}O_2$	Negative	$[M-H]^-$	413 → 369	100	5
PFAS	FBSA	$C_4F_9SO_2NH_2$	Negative	$[M-H]^-$	298 → 78	150	20
PFAS	FHxSA	$C_6F_{13}SO_2NH_2$	Negative	$[M-H]^-$	398 → 78	200	25
PFAS	FOSA	$C_8F_{17}SO_2NH_2$	Negative	$[M-H]^-$	498 → 78	250	30
PFAS	GenX	$C_6HF_{11}O_3$	Negative	$[M-H]^-$	285 → 169	100	5
PFAS	MeFOSA	$C_9H_4F_{17}NO_2S$	Negative	$[M-H]^-$	512 → 169	150	35
PFAS	EtFOSAA	$C_{12}H_8F_{17}NO_4S$	Negative	$[M-H]^-$	584 → 419	100	5
PAEs	DMP	$C_{10}H_{10}O_4$	Positive	$[M+H]^+$	195 → 163	175	15
PAEs	DEP	$C_{12}H_{14}O_4$	Positive	$[M+H]^+$	223 → 207	175	8
PAEs	DBP	$C_{16}H_{22}O_4$	Positive	$[M+H]^+$	279 → 149	175	5
PAEs	BBP	$C_{19}H_{20}O_4$	Positive	$[M+H]^+$	313 → 91	175	5
PAEs	DEHA	$C_{22}H_{42}O_4$	Positive	$[M+H]^+$	371 → 355	300	8
PAEs	DNOP	$C_{24}H_{38}O_4$	Positive	$[M+H]^+$	391 → 149	250	5
OPEs	TCEP	$C_6H_{12}Cl_3O_4P$	Positive	$[M+H]^+$	285 → 269	250	20
OPEs	TCPP	$C_9H_{18}Cl_3O_4P$	Positive	$[M+H]^+$	327 → 215	250	30
OPEs	TDCPP	$C_9H_{15}Cl_6O_4P$	Positive	$[M+H]^+$	431 → 415	300	25
PAHs	ACY	$C_{12}H_8$	Positive	$[M]^+$	152 → 150	250	40
PAHs	ACE	$C_{12}H_{10}$	Positive	$[M]^+$	154 → 152	250	30
PAHs	PHE/ANT	$C_{14}H_{10}$	Positive	$[M]^+$	178 → 152	250	40
PAHs	FLE	$C_{13}H_{10}$	Positive	$[M]^+$	166 → 165	250	30
PAHs	PYR/FLA	$C_{16}H_{10}$	Positive	$[M]^+$	202 → 200	200	60

Data analysis

Mass spectra were analyzed using Agilent MassHunter Qualitative Analysis 12.0. An in-house library was first established using standard compounds. For each target, the most abundant and characteristic product ions were selected. The method-specific accurate mass spectra were compiled using the MassHunter Personal Compound Database and Library Manager. The library was then used for targeted screening using the PRM data. The MassHunter Molecular Structure Correlator program correlated accurate mass MS/MS fragment ions with one or more proposed molecular structures. Publicly available databases (Massbank and PubChem) were also used to confirm the proposed formulas.

For quantification, quantitative product ions were extracted with a 5 ppm mass tolerance window. Matrix-matched calibration curves (from 0 to 100 ng/g) for each analyte were generated by plotting peak area ratios of target analytes to their respective isotopically labeled internal standards against concentration ratios.

Results and discussion

Accurate mass measurement is important for unambiguous compound identification when developing a new methodology. The mass accuracy was monitored over three days for targets of different compound classes. The mass errors were all maintained below 0.2 ppm as shown in Table 4. The results demonstrated excellent mass accuracy of the SICRIT platform combined with the Revident LC/Q-TOF instrument. The quantification performance was assessed by linearity, limit of detection (LOD), and limit of quantification (LOQ). Linearity was determined by the coefficient of determination (R^2). The LOD is determined by a peak with a signal to noise ratio of 3. The LOQ is determined by a peak with a signal-to noise ratio of 10. Reproducibility assessments (n = 5) were applied to ensure data accuracy and reliability. The data were summarized in Table 5, showing excellent linearity ($R^2 > 0.995$), LOD, and LOQ for all targets.

ISF of PFAS is unavoidable during ESI in traditional LC-ESI-MS analysis. This greatly reduces the response of molecular ions and may also result in errors of identification. While analyzing real samples, there may be potential ion suppression or enhancement effect during ionization process, affecting the fragmentation pathway and extent. Thus, low ISF is crucial for accurate PFAS quantification, especially when the sample matrix is complex. Combining SICRIT with the Revident LC/Q-TOF provided enhanced analytical and quantification performance through soft ionization. Table 6 summarizes the ISF ratio of PFAS, which was calculated by dividing the peak area of an individual ISF ion by the sum of the peak areas of the molecular ion and all ISF ions. Except for GenX, the ISF ratios were all below 20%, while recent studies revealing the fragmentation behaviors of PFAS using LC-ESI-MS demonstrated more than 60% of fragmentation.[3] Our platform plasma-based ionization offered superior ionization efficiency and significantly increased spectral interpretability, facilitating reliable PFAS identification in complex sample matrices.

Table 6. The in-source fragmentation ratios of PFAS analyzed by dielectric barrier discharge ionization high-resolution mass spectrometry.

Target	Fragmentation Ratio (%)
TFA	13
PFPrA	13
PFBA	19
PFPeA	12
PFHxA	8
PFOA	2

Target	Fragmentation Ratio (%)
FBSA	0
FHxSA	0
FOSA	0
GenX	68
MeFOSA	1
EtFOSAA	6

Table 4. Interday mass accuracy of targets from different compound classes.

Compound Class	Target	Mass Error (ppm)		
		First Day	Second Day	Third Day
PAHs	FLE	0.01	0.01	0.01
PAHs	PHE/ANT	0.01	0.01	0.01
PAEs	DMP	0.08	0.08	0.08
PAEs	DBP	0.05	0.05	0.05
OPEs	TCEP	0.16	0.16	0.16
OPEs	TDCPP	0.00	0.00	0.00

Table 5. Quality parameters of the Plasmion SICRIT-Agilent Revident LC/Q-TOF method for PFAS, PAE, OPE, and PAH analysis.

Targets	R^2	LOD (pg/m^3)	LOQ (pg/m^3)
TFA	0.996	0.19	0.64
PFPrA	0.997	0.18	0.58
PFBA	0.9955	0.77	2.58
PFPeA	0.9962	2.02	6.72
PFHxA	0.9958	1.69	5.65
PFOA	0.9965	6.97	23.25
FBSA	0.9968	0.06	0.2
FHxSA	0.9959	0.14	0.47
FOSA	0.9961	0.23	0.76
GenX	0.9963	0.16	0.53
MeFOSA	0.996	0.15	0.49
EtFOSAA	0.9957	0.32	1.08
DMP	0.9964	0.04	0.14
DEP	0.9956	0.03	0.1
DBP	0.9962	0.05	0.16
BBP	0.9959	0.88	2.95
DEHA	0.9961	0.36	1.22
DNOP	0.9958	3.44	11.48
TCEP	0.9957	3.95	13.17
TCPP	0.996	1.39	4.64
TDCPP	0.9956	0.55	1.83
ACY	0.9958	0.76	2.53
ACE	0.9959	1.08	3.61
PHE/ANT	0.996	0.41	1.38
FLE	0.9957	0.65	2.15
PYR/FLA	0.9958	0.82	2.73

After development and validation of the method, PM$_{2.5}$ samples, complex environmental matrices containing numerous airborne contaminants, were used to showcase its capability. Figure 3 reveals the ubiquitous presence of the target pollutant classes, with distinct phase partitioning and seasonal variations.

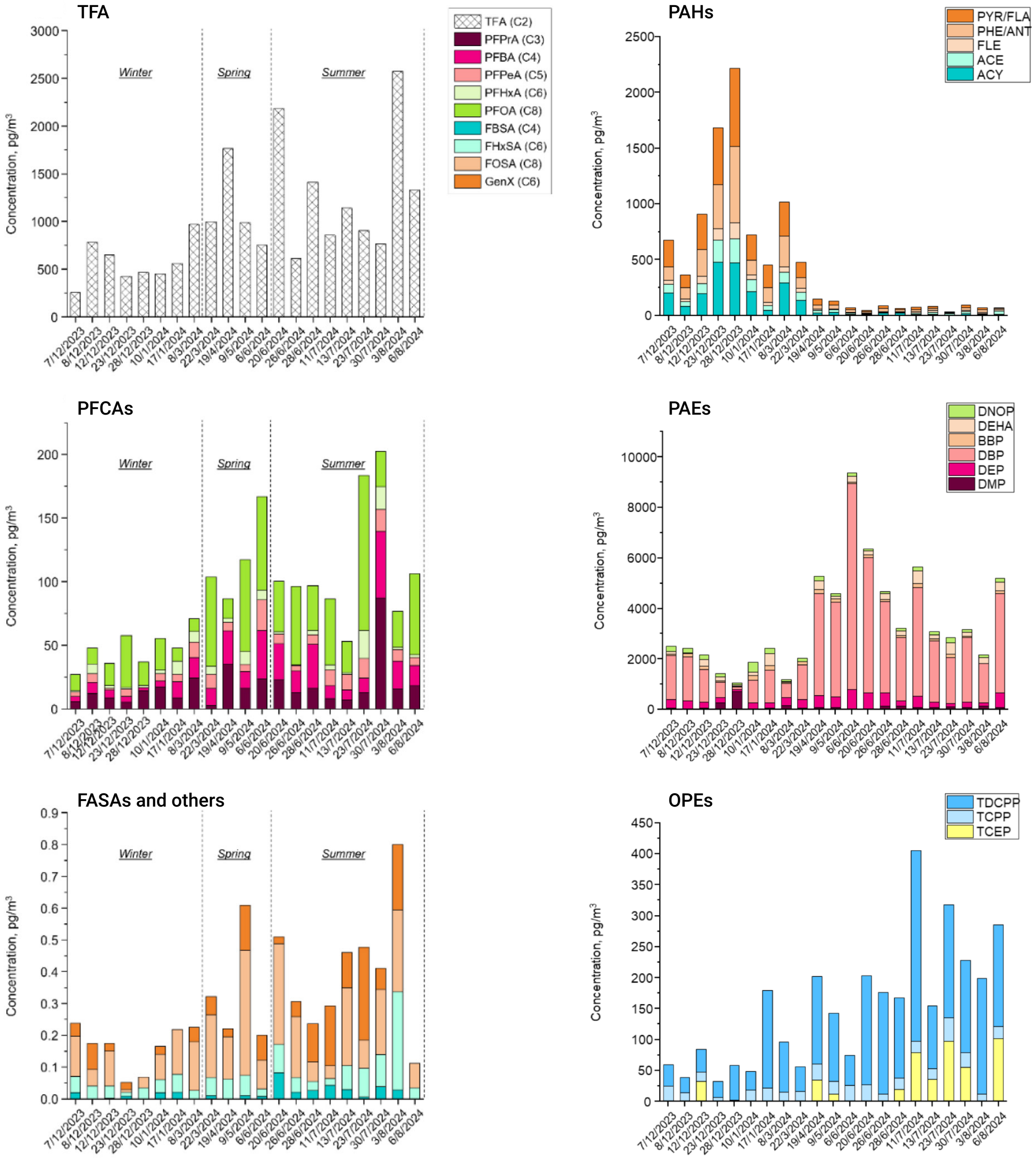

Figure 3. Seasonal variations of the concentrations of TFA, PFCA, PAH, PAE, OPE, FASA, and others detected in PM$_{2.5}$ collected in Zhengzhou from December 2023 to August 2024.

Conclusion

In this application note, the Plasmion SICRIT platform combined with the Agilent Revident LC/Q-TOF instrument demonstrated outstanding performance for the simultaneous analysis of diverse environmental contaminants in complex matrices using soft- and broad-spectrum ionization. The system delivered excellent mass accuracy with errors consistently below 0.2 ppm across multiple compound classes over three days, ensuring reliable compound identification. Superior quantification performance was achieved with excellent linearity ($R^2 > 0.995$), low limits of detection and quantification, and high reproducibility. Most importantly, the platform significantly minimized ISF of PFAS, with ISF ratios below 20% for most targets, which was substantially lower than the > 60% typically observed with conventional LC-ESI-MS. This approach enhanced molecular ion response, improved spectral interpretability, and reduced matrix effects through solvent-free analysis, enabling more accurate identification and quantification even in challenging environmental samples. Application to real $PM_{2.5}$ samples successfully revealed the widespread occurrence, phase partitioning, and seasonal variations of target pollutants, highlighting the platform's robustness and suitability for advanced environmental monitoring.

References

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DE-014050

Printed in the USA, April 21, 2026
5994-9153EN

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