



Research Paper

Rapid detection of per- and polyfluoroalkyl substances (PFAS) using paper spray-based mass spectrometry

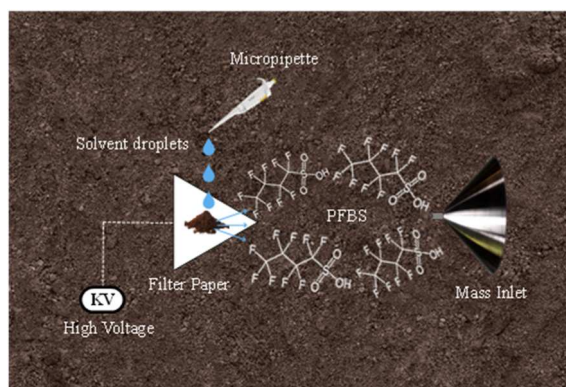
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HIGHLIGHTS

- Developed a simple, inexpensive, sensitive and rapid PFAS detection based on PS-MS and DPS-MS.
- Food packaging paper can be cut and directly analyzed for PFAS contamination by PS-MS in less than 1 min.
- Soil sample in a small amount can be directly analyzed by DPS-MS for PFAS identification, with no sample preparation.

GRAPHICAL ABSTRACT



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ABSTRACT

Traditional PFAS analysis by mass spectrometry (MS) is time-consuming, as laborious sample preparation (e.g., extraction and desalting) is necessary. Herein, we report fast detection of PFAS by paper spray (PS)-based MS techniques, which employs a triangular-shaped filter paper for sample loading and ionization (≤ 3 min per sample). In this study, PS-MS was first used for direct PFAS analysis of drinking water, tap water, and wastewater. Interestingly, food package paper materials can be directly cut and examined with PS-MS for possible PFAS contamination. For samples containing salt matrices which would suppress PFAS ion signal, desalting paper spray mass spectrometry (DPS-MS), was shown to be capable of rapidly desalting, ionizing and detecting PFAS species such as per-fluorooctanoic acid (PFOA) and per-fluorosulphonic acid (PFOS). The retention of PFAS on paper substrate while salts being washed away by water is likely due to hydrophilic interaction between the PFAS polar head (e.g., carboxylic acid, sulfonic acid) with the polar filter paper cellulose surface. The DPS-MS method is highly sensitive (limits of detection: 1.2–4.5 ppt) and can be applicable for directly analyzing soil extract and soil samples. These results suggest the high potential of PS-MS and the related DPS-MS technique in real-world environmental analysis of PFAS.

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1. Introduction

Per- and poly-fluoroalkyl substances (PFAS), widely recognized as “forever chemicals” [1], are a class of organic substances in which backbone hydrogens are substituted with fluorine atoms [2,3]. Per-fluoroalkyl chains (C_nF_{2n+1}) with polar heads (e.g., CO_2 , SO_3) are a common structural feature of PFAS molecules [4]. PFAS are man-made chemicals with unique surfactant properties and oil/water repellency and have been used in manufacturing, consumer, and industrial products since the 1960 s [5,6]. PFASs are very stable due to the high C-F bond energy ($531.5 \text{ kJ.mol}^{-1}$), making them resistant to degradation and environmentally persistent [7,8]. Organization for Economic Cooperation and Development (OECD) global database reveals that more than 4700 PFAS-related CAS numbers are identified, having manifold physicochemical properties [9]. Based on the recently revised definition of PFAS to include any chemical containing at least one saturated CF_2 or CF_3 moiety, PubChem, one of the largest open chemical collections, now contains over 7 million PFAS [10]. Among commonly found PFAS species, PFOA and PFOS are of great concern within this family of compounds because of their persistence, toxicity, and potential bioaccumulation in the environment [11]. From a regulatory point of view, PFOA and PFOS have been included by the Stockholm Convention as persistent organic pollutants in Annex A and B, suggesting their eradication and production restrictions [12–14]. These compounds have been linked to several health issues. Exposure to PFOA and/or PFOS causes adverse effects on fetus development, e.g., decreased birth weight. The non-cancer effect of updated health advisories for PFOA and PFOS is the suppression of vaccine response, causing a decrease in serum antibody concentrations in children [12].

Recent reports disclose that PFAS are present in different matrices such as food, water, biological samples, and soil [15–17] with varying levels (e.g., 1 ppt to 237 ppb) [12,18–20]. For example, the study of PFAS in food packaging materials and soils are given lots of attention. Packaging has become a crucial aspect of food manufacturing as it serves several vital purposes: safeguarding food from external factors, enabling preservation and convenient transportation, and furnishing consumers with information about ingredients and nutrition [21,22]. Over recent years, there has been a substantial increase in the production and utilization of packaging materials to meet the substantial demand in the food industry. Remarkably, food packaging now constitutes nearly two-thirds of the overall volume of packaging waste [21]. While the packaging manufacturing sector endeavors to create materials that minimize environmental impact while ensuring food safety, there has been a growing concern regarding packaging as a potential source of food contamination. This is primarily due to substances migrating from the packaging into the food [23]. Among the various harmful chemicals identified in recent research [24], fluorochemical compounds have emerged as a significant concern in terms of food safety. This is because they are extensively employed as coatings on food packaging to repel grease and water [24]. Also, PFAS is often found in soil. Soil is a complex matrix with various organic and inorganic components.

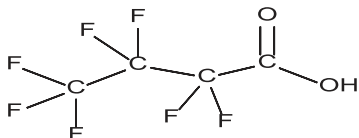
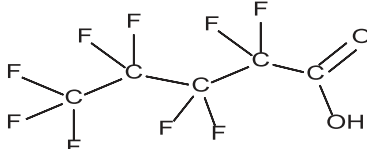
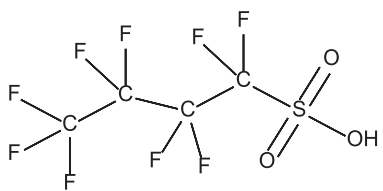
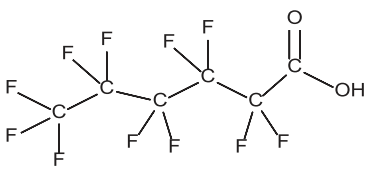
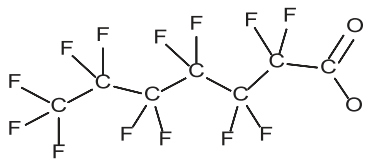
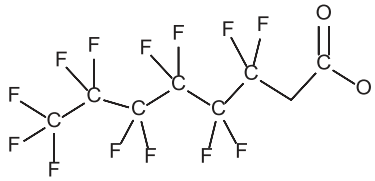
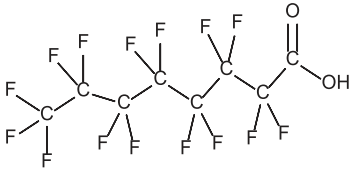
Due to the complexity and variety of sample matrices, the detection of PFAS typically requires sample preparation and/or pretreatment before analysis. Solid phase extraction (SPE), solid phase micro-extraction (SPME), liquid-liquid extraction (LLE), and dispersive liquid-liquid microextraction (DLLME), are extraction techniques commonly reported to remove sample matrices and to preconcentrate samples prior to analysis but ended up with low recovery yields of analytes and false negative results in trace analyses [25–27]. Due to the demand for high sensitivity and low limit of detection (LOD) for trace analysis of PFAS, liquid chromatography (LC) coupled with electrospray ionization-tandem mass spectrometry (ESI-MS/MS) or high-resolution mass spectrometry (HRMS) is mostly used after sample pretreatment for targeted and non-targeted analyses [28,29]. LC/MS provides a foundation for PFAS analysis but possesses several drawbacks. Time-consuming LC separation step, excessive solvent consumption and

generation of large amounts of chemical waste forge LC techniques uncooperative to high-throughput analyses, given that separation times were on the magnitude of tens of minutes [28–30]. Second, another grand challenge for PFAS analysis of environmental samples by MS is the ion signal suppression by matrix. Thus, the matrix needs to be removed before MS analysis. This can be done by extraction and/or desalting prior to MS analysis [31], but it would also take time. For instance, for analyzing PFAS coated packaging material, specially microwaved popcorn paper, Zabaleta et al., mentioned burdensome extraction procedure [32]. The procedure demands cutting the paper into a certain size (1 dm^2) and soaked in a vessel containing methanol. After soaking the paper requires sonication and then evaporation to dryness. After that, the sample was reconstituted for subsequent LC/MS analysis. The whole process is time consuming. Likewise, sample preparation for LC/MS analysis of PFAS in soil samples is also troublesome. It is time-consuming due to the intricate extraction and cleanup processes involved, which is labor-intensive and requiring substantial manual effort. Moreover, the specialized consumables and equipment required, such as SPE cartridges and solvents, add to the financial burden of PFAS analysis. Achieving the necessary sensitivity for PFAS detection can be challenging, especially when dealing with complex sample matrices or low-level PFAS compounds. Simon et al. reported SPE method to extract organically bound fluorine (EOF) from soil samples and quantified by high resolution-continuum source-graphite furnace molecular absorption spectrometry (HR-CS-GFMS). The procedural LOD was shown to be $3.43 \text{ } \mu\text{g/kg}$ (3.43 ppb) [31]. Yeung et al. did similar studies and quantified PFOS present in the surface and core sediment of near Lake Ontario using LC/MS method, in which LOD for PFOS was found to be $30.1 \text{ } \mu\text{g/kg}$ (30.1 ppb) [33]. Rankin et al. reported PFAS soil concentrations for a single sampling site located in Antarctica. After collecting the soil sample extraction experiment was performed where they primarily mixed the soil with methanol in centrifuge tube. Then they added sodium hydroxide and ACN: water (90:10) for vortexing (15 ~ 30 s) and then sonicated for 60 min in an ice bath. After extraction the sample was passed to SPE manifold. PFOA and PFOS concentrations were measured to be 0.05 and $0.007 \text{ } \mu\text{g/kg}$ (50 ppt and 7 ppt), respectively, as analyzed by LC/MS/MS [34,35]. Recently, a 3D-printed cone ionization strategy was reported for in situ analysis of per- and polyfluoroalkyl substances in soils and sediments, where 1 g sample was deposited the cone cavity. PFAS was extracted and eluted by adding 1 mL of methanol to the cone for spray ionization with -5.75 kV high voltage. The method showed LOD at 100 ppt level. In that study, cone clogging was a challenge after sample deposition [6].

Paper spray mass spectrometry (PS-MS) [36–38], pioneered by Cooks, Ouyang, and their colleagues, offers a rapid and direct analytical technique that requires minimal or no purification steps. PS-MS has gained prominence as one of the most extensively employed ambient ionization methods for analyzing a diverse range of compounds, including drugs, peptides, proteins, reaction intermediates, various food components, metabolites, and environmental pollutants [39–47]. However, few studies for PFAS analysis by PS-MS were reported. Sero et al. reported an analysis of fluorotelomer alcohols (FTOHs), fluorooctane sulfonamides (FOSAs) and fluorooctane sulfonamido-ethanols (FOSEs) by photoionization paper spray where a high energy UV-krypton light beam was installed to ionize the sample. The most intense ions observed in the mass spectra were $[M-H]^-$ for FOSAs and $[M+O_2]^-$ for FTOHs and FOSEs, respectively, and the quantitation sensitivity of mg.L^{-1} (or ppm) was reported [13]. Therefore, an effective MS method based on paper spray (PS) with enhanced speed and sensitivity would be desirable for PFAS analysis. In this study, we first showed the rapid detection of PFAS from environmental water samples by PS-MS (e.g., tap water, drinking water and wastewater; ca. 2 min per sample analysis). To examine PFAS contaminant of food packaging materials, PS-MS can be directly applied, in which packaging material is cut into a triangular shape paper substrate for PFAS analysis (ca. 1 min per sample). In addition, for PFAS samples containing complicated matrices (e.

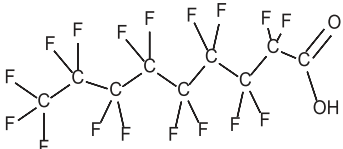
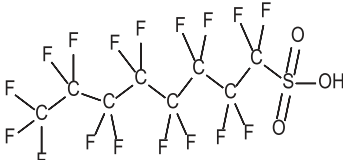
Table 1

Observed fragment ions of PFAS ions from standard PFAS samples upon CID.

PFAS	Structures	Precursor ions	Precursor ions (m/z)	Fragment ions
PFBA		$C_3F_7COO^-$	212.9	C_3F_7 (m/z 168.9), C_2F_5 (m/z 118.9)
PFPeA		$C_4F_9COO^-$	262.9	C_4F_9 (m/z 218.9), C_3F_7 (m/z 168.9), C_2F_5 (m/z 118.9)
PFBS		$C_4F_9SO_3^-$	298.9	C_4F_9 (m/z 218.9), C_3F_7 (m/z 168.9), C_2F_5 (m/z 118.9), FSO_3^+ (m/z 98.9), SO_3^+ (m/z 79.9)
PFHxA		$C_5F_{11}COO^-$	312.9	C_5F_{11} (m/z 268.9), C_2F_5 (m/z 118.9)
PFHpA		$C_6F_{13}COO^-$	362.9	C_6F_{13} (m/z 318.9), C_3F_7 (m/z 168.9), C_2F_5 (m/z 118.9)
6:2FTCA		$C_6F_{13}CH_2COO^-$	376.9	C_7F_{11} (m/z 292.9)
PFOA		$C_7F_{15}COO^-$	412.9	C_7F_{15} (m/z 368.9), C_4F_9 (m/z 218.9), C_3F_7 (m/z 168.9), C_2F_5 (m/z 118.9)

(continued on next page)

Table 1 (continued)

PFAS	Structures	Precursor ions	Precursor ions (m/z)	Fragment ions
PFNA		$C_8F_{17}COO^-$	462.9	C_8F_{17} (m/z 418.9), C_5F_{11} (m/z 268.9), C_4F_9 (m/z 218.9), C_3F_7 (m/z 168.9), C_2F_5 (m/z 118.9)
PFOS		$C_8F_{17}SO_3^-$	498.9	C_8F_{17} (m/z 418.9), $C_6F_{12}SO_3^+$ (m/z 379.9), C_6F_{13} (m/z 318.9), C_5F_{11} (m/z 268.9), C_4F_9 (m/z 218.9), C_3F_7 (m/z 168.9), C_2F_5 (m/z 118.9)

g., salts, soils) which would cause ion suppression, enhanced detection sensitivity was achieved by desalting paper spray mass spectrometry (DPS-MS) [37,38], a PS-based method which integrates the desalting step with the ionization step for fast chemical analysis (ca. 3 min per sample). The rationale for using DPS-MS in this case is that the regular filter paper consists of hydrophilic cellulose [37] and PFAS contains polar heads of COO^- or SO_3^- . We reason that there would be strong interactions between the PFAS molecules and the paper substrate. Thus, one could deposit the sample onto the paper substrate and apply water to rinse away the non-volatile salt matrix while keeping PFAS retained on the paper for subsequent paper spray ionization. As a result, we successfully demonstrated the analysis of PFAS in different salt matrices as well as the rapid PFAS detection from soil extract and soil samples by DPS-MS.

2. Experimental section

2.1. Material

Per-fluorobutanoic acid (PFBA, CAS No. 375–22-4), Per-fluoropentanoic acid (PFPeA, CAS No. 2706–90-3), Per-fluoroheptanoic acid (PFHpA, CAS No. 375–85-9), Per-fluorononanoic acid (PFNA, CAS No. 375–95-1), PFOA (CAS No. 335–67-1), PFOS (CAS No. 1763–23-1), per-fluorohexanoic acid (PFHxA, CAS No. 307–24-4), per-fluorobutanesulfonic acid (PFBS, CAS No. 375–73-5) were purchased from Sigma-Aldrich (St. Louis, MO, USA; Structures are shown in Table 1). 2H, 2H-Perfluorooctanoic acid (6:2 FTCA, CAS No. 53826–12-3) was purchased from Synquest Laboratories (Alachua, FL). Potassium chloride, sodium chloride, sodium sulfate, HPLC-grade acetonitrile, and methanol were obtained from Fisher Scientific (Waltham, MA, United States). Deionized water was from EMD Millipore (Burlington, MA, United States). A Fisher brand p8 filter paper was purchased from Fisher Scientific Co. and used in our PS-MS and DPS-MS experiments. Stock solutions of 1 mM PFOA, PFOS, PFHxA and PFBS were prepared by dissolving solid compounds in a solvent of methanol: water (20:80). Working samples were prepared by diluting a suitable volume of stock solution using water. 50 μ M of PFOA solution was used as a test sample to optimize the DPS-MS condition. Great Value microwave popcorn paper and Beef Pho Instant Noodle's were purchased from the local Walmart store. McDonalds burger wrapper, Burger King wrapper and burger king French fry box were collected from corresponding local restaurants.

2.2. Soil sample collection and extraction

Soil sample was collected in the Keegan landfill area of New Jersey

on April 13, 2022. Soil sample was collected around 0.05 m deep below the ground using steel shovel. 5 g of sample was transported from the sampling location to laboratory by filling into Ziploc bag. 3 g of soil sample was measured, finely grinded and transferred to 20 mL glass bottle and 2 mL water was added to extract and concentrate possible PFAS contaminants. The sample was then further sonicated for 1 min in a water bath to extract PFAS.

2.3. Wastewater sampling

The wastewater sample was obtained from an anonymous location and thus sampling location is not included in this work due to confidentiality agreement. The sample was stored in high density polyethylene (HDPE) to prevent the loss of PFAS to the container, or contamination of the sample with PFAS. It was placed in a cooler on ice at 4 °C during transportation and was maintained at 4 °C until analysis [48].

2.4. Apparatus

A high-resolution Q Exactive Orbitrap mass spectrometer (Thermo Scientific, San Jose, CA, USA) was used to conduct MS and MS/MS experiments. The instrument underwent calibration on a weekly schedule. Calibration was performed using a commercially accessible solution, Pierce™ ESI Negative Ion Calibration Solution, obtained from Thermo Scientific. The commercial ESI ion source was removed to accommodate our paper spray (PS), desalting paper spray (DPS), and nano electrospray ionization (nanoESI) ion sources. The capillary inlet temperature was set to 250 °C. Data analysis was acquired by Thermo Xcalibur (3.0.63). To conduct collision-induced dissociation (CID) MS/MS experiment, 10–45 normalized collision energy (NCE) was used. Instruments parameters such as AGC target, microscan and maximum injection time were adjusted based on relative abundance of detected PFAS ions. In general, AGC target was selected from $2E4 \sim 1E6$, microscans 3 $\sim$ 8 and maximum injection time was set from 30 $\sim$ 1000 ms. For the LC/MS experiment as a comparison, a Waters ultra-performance liquid chromatography (UPLC, Milford, MA, USA) system equipped with a C_{18} column was used for LC/MS experiment for separation and detection of PFAS. 10 mM ammonium acetate and methanol were used as mobile phase A and B, respectively. The elution gradient was run for 18 min to separate PFAS species at the flow rate of 0.3 mL/min.

2.5. SEM and EDX

Scanning electron microscopy (SEM) analysis was performed on EM JSM-7900 F, JEOL operated at 15 kV to characterize the surface

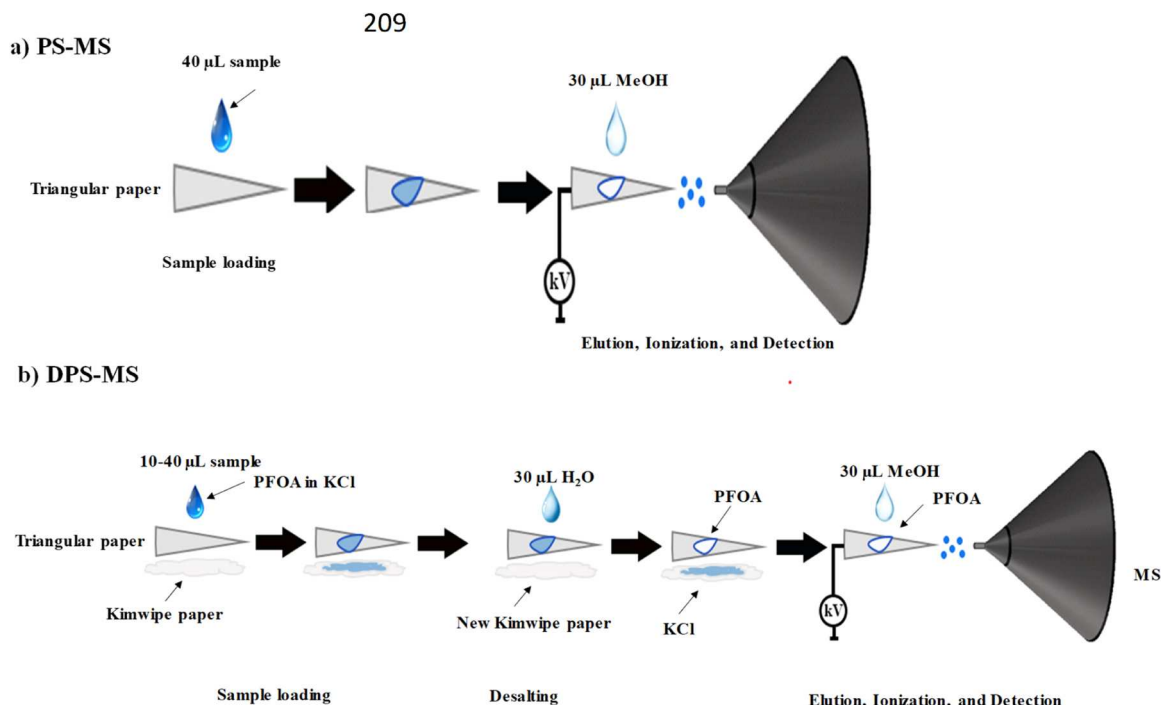


Fig. 1. Schematics showing the apparatus and workflows of a) PS-MS and b) DPS-MS.

morphology. SEM micrograms of target sample were taken at x200 magnification. Energy-dispersive X-ray spectroscopy (EDX) was used to analyze the elemental composition of the paper substrate before and after loading PFAS.

2.6. PS-MS analysis

To conduct PS-MS [39,49,50] analysis, the Fisher brand qualitative p8 filter paper was cut into triangle shapes. Triangular shape filter paper (10 mm $\times$ 5 mm, height $\times$ width) was sonicated sequentially by acetone, methanol, and methanol/water (50:50 v/v, 15 min each). Sample solution ($\sim$ 40 μL) was dropped onto the triangular paper substrate. After drying, the paper triangle was then held in front of the MS inlet (8 mm away, see apparatus shown in Fig. 1a; picture is shown in Fig. S1) and 30 μL of MeOH (100%) was added directly onto the paper triangle to elute target compounds for ionization upon application of a high voltage (-3.5 kV) to the wetted paper.

To analyze food packaging materials, the packaging material paper was cut into triangles (10 mm $\times$ 5 mm, height $\times$ width) and held in front of the MS inlet (8 mm away). 30 μL of MeOH (100%) was added directly onto the paper triangle to direct extract and elute compounds for ionization upon application of a high voltage (-3.5 kV).

2.7. DPS-MS analysis

In this DPS-MS experiment, the Fisher brand qualitative p8 filter paper (Fisher Scientific) was cut and cleaned in the same way as in the PS-MS experiment. As shown in Fig. 1b, a 10 μL sample solution was spotted onto the cleaned paper triangle placed on top of a Kimwipe to facilitate the absorption by capillarity (in some cases, 10 μL of sample was added 4 times onto the paper substrate to enhance the detection sensitivity) [51]. Desalting was achieved by loading 30 μL of ultrapure H_2O (10 μL of H_2O each time, three time loadings) onto the paper placed on top of another Kimwipe (to help suck the loaded water) to wick the sample salts and other matrix chemicals. The paper triangle was then held in front of the MS inlet (8 mm away) using a high-voltage cable with an alligator clip, and 30 μL of MeOH (100%) solution was drenched

with the paper triangle to elute the target compounds for spray ionization upon application of a high voltage (-3.5 kV) to the wetted paper.

2.8. nanoESI-MS analysis

A pulled fused-silica capillary with a conical tip (i.d., $\sim$ 1 μm) was produced using a laser puller (model P1000, Sutter Instrument Inc, USA). Sample solution was directly infused into the pulled fused-silica capillary at a flow rate of 2 $\mu\text{L}/\text{min}$ using a syringe driven by a syringe pump. The capillary was placed 8 mm distance from the mass spectrometer inlet, and high voltage (-3.5 kV) was applied to the syringe needle for triggering ionization.

3. Results and discussion

As PFAS occurs in trace level in complicated matrices, a method with high sensitivity, high specificity and fast analysis speed would be needed. We considered the PS-based MS approach because it is highly sensitive and fast as it involves minimum sample preparation. Also, high resolution MS measurement provides accurate mass for PFAS identification with high specificity. In this study, we adopted PS-MS for analyzing environmental water samples and food packaging paper materials. In addition, we also attempted DPS-MS for soil samples and samples with salt matrices.

3.1. PFAS analysis by PS-MS

3.1.1. Water sample analysis by PS-MS

First, we explored the application of our PS-MS (see apparatus in Fig. 1a) for the analysis of PFAS in water samples. As PFAS is ubiquitous, care was first taken to ensure no PFAS signal was seen from the blank control experiment. In our blank control experiment, a triangular-shaped blank paper was examined for cross-contamination of the most pervasive PFOA, PFOS, PFHxA and PFBS. For this experiment we attached a blank paper to a high voltage alligator clip which was aligned and pointed to the mass inlet and 30 μL of MeOH was added directly to the blank paper to extract any of the mentioned PFAS for ionization and

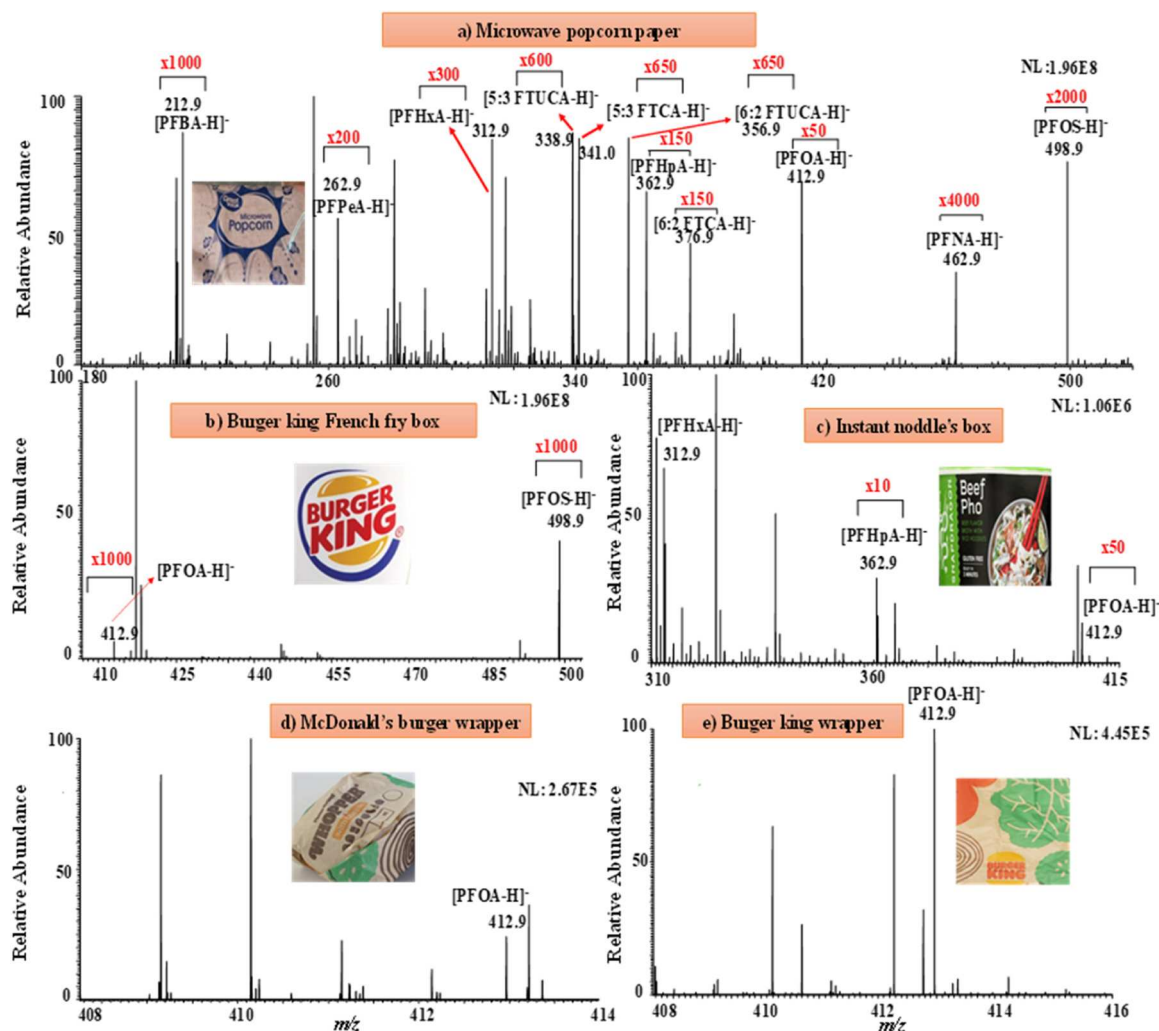


Fig. 2. Negative ion mode PS-MS spectra of a) Microwave popcorn paper, b) Burger King French fry box, c) Instant noodles box (Beef Pro), d) McDonalds burger wrapper, and e) Burger King wrapper. Various PFAS including PFBA, PFPeA, PFHxA, 5:3 FTCA, 5:3 FTUCA, 6:2 FTUCA, PFHpA, 6:2 FTCA, PFOA, PFNA and PFOS were found in these food packaging materials.

detection. No PFOA, PFOS, PFHxA and PFBS were seen from this control experiment (MS spectrum shown in Fig. S2). To conduct water analysis, water samples were collected from three different locations: Harrison City (Harrison, NJ), New Jersey Institute of Technology (Newark, NJ), and an anonymous location. After collecting water, a 10 μ L sample was added to the paper substrate four times, and we waited 30 s until it dried. As shown in the acquired MS spectra (Fig. S3b-c), PFOA with low intensity was detected in both Harrison and NJIT tap water samples (mass error <2.6 ppm), while no PFOA was observed in a blank sample (Fig. S3a). Interestingly, no PFOA was found in NJIT fountain water Fig. S3d, probably because of the filtration system.

In addition, for the wastewater from an anonymous location, different PFAS compounds such as PFOA (measured m/z 412.96591, theoretical m/z 412.96643, mass error: -1.3 ppm), PFOS (measured m/z 498.942952, theoretical m/z 498.93022 and mass error: -1.4 ppm), PFHxA (measured m/z 312.97248, theoretical m/z 312.97281, mass error: -1.1 ppm), PFBS (measured m/z 298.94254, theoretical m/z 298.94299, mass error: -1.5 ppm) and perfluorohexane sulfonic acid (PFHxS, measured m/z 398.93624, theoretical m/z 398.93660, mass error: -0.9 ppm) were observed, as shown in the acquired mass spectrum of the corresponding analysis (Fig. S4). This result indicates the power of PS-MS for analysis of different water samples in a short period of time (ca. 2 min per sample).

To test the accuracy of our PS-MS method for PFAS detection, we

spiked the NJIT lab tap water sample with low concentrations of PFBS, PFHxA and PFOS (100 ppt each). This lab tap water sample only contained PFOA before spiking (Fig. S3-b). After spiking, we successfully detected all three spiked PFAS along with the pre-existing PFOA by PS-MS, which suggests the reliability and accuracy of our PS-MS detection of PFAS in real samples. In comparison, we also ran LC/MS for the spiked tap water sample. Although all three spiked PFAS along with PFOA were detected by LC/MS, their ion intensities from LC/MS were lower than PS-MS (Fig. S5). In particular, the ion intensities for PFOS and PFOA from LC/MS was lower than those of PS-MS by 10 and 88 folds, respectively. This result shows the strength of PS-MS for the detection of trace amount of PFAS in real samples.

3.1.2. Food packaging sample analysis by PS-MS

We further examined the direct analysis of PFAS contamination in food packaging material using PS-MS. In this experiment, food packaging material papers were cut into triangular shapes, to serve as paper spray emitters. To extract and ionize PFAS contained in the paper material, MeOH (100%) was added onto the paper. This process was rapid, completed in less than 1 min. The process is similar to the previously reported leaf spray [52] technique. In our experiment, we examined five commercially available food packaging papers in different brands and identified several different classes of PFAS such as per-fluorocarboxylate, per-fluorosulfonate and fluorotelomer

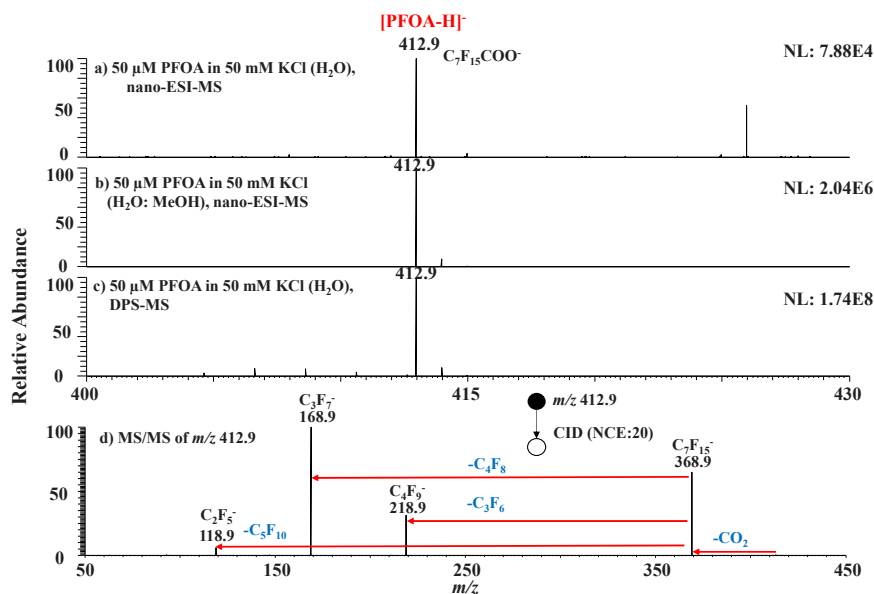


Fig. 3. Negative ion mode MS spectra of 50 μM PFOA in 50 mM KCl were collected using a) nanoESI-MS (no MeOH was added), b) nanoESI-MS (MeOH was added), and c) DPS-MS. d) CID MS/MS spectrum of the PFOA ion $\text{C}_7\text{F}_{15}\text{COO}^-$ at m/z 412.9.

unsaturated carboxylate. The primary purpose of using them in food packaging paper is to provide protection against grease, moisture, heat, and to ensure that the packaging is safe to the food. The identified PFAS compounds including PFBA, PFPeA, PFHxA, 5:3 FTCA, 5:3 FTUCA, 6:2 FTUCA, PFHpA, 6:2 FTCA, PFOA, PFNA, and PFOS as illustrated in Fig. 2 were confirmed by their accurate masses (mass error < 5 ppm, Table S1, Supporting Information) and collision-induced dissociation (CID) analysis (see MS/MS data listed in Table S1, Supporting Information). The corresponding EIC spectra of these observed PFAS ions (shown in Fig. 2) are illustrated in Fig. S6. Upon CID, the fragmentation of these PFAS ions (shown in Fig. 2) occurs mainly via C-C or C-F cleavages or by losses of CO_2 or SO_3 (fragment ions are summarized in Table S1), which is in agreement with ion dissociation behaviors of PFAS ions generated from standard PFAS samples (MS/MS results are summarized in Table 1; MS spectra of PFAS ions from standard samples are also shown in Fig. S7). Interestingly all the papers contained different types of PFAS. In particular, Popcorn paper contained the most varieties of PFAS compounds (Fig. 2a). It was observed that PFOA is ubiquitous and found in all the tested samples. Results from McDonalds wrapper (Fig. 2d) and Burger King French fry box (Fig. 2e) showed the existence of PFOA with reasonable intensity ($1\text{E}4 \sim 1\text{E}5$), but Berger King French fry box (Fig. 2b) contained both classes of shorter chain PFAS (perfluoro carboxylate and perfluoro sulphonate). Furthermore, we identified three shorter chain PFAS (PFHxA, PFHpA and PFOA) from Instant noodles box container (Fig. 2c). Recently, Indiana environmental organization outreached similar news and Huang et al. [53]. reported the presence of PFAS in ice tea, instant noodle and bubble tea container. Herein, our study demonstrated the power of PS-MS in PFAS analysis, which is quite fast as no sample preparation is needed (ca. 1 min per sample).

3.2. PFAS analysis by DPS-MS

In some preliminary tests of PS-MS experiments, we also found the signal suppression effect for samples containing high level of non-volatile salt matrices. To solve this problem, we added one “on-paper” desalting step for PS-MS, namely DPS-MS, for PFAS analysis, as described below. DPS-MS was shown to be effective in analyzing glycans and glycopeptides in the presence of salts [37,38].

3.2.1. Optimization of DPS-MS

Effort was first made for DPS-MS signal optimization, using 50 μM PFOA solution prepared in 50 mM KCl as the test sample, as the ion signal from DPS ionization could be influenced by various factors (e.g., the distance between the paper tip and the mass inlet, the volume of the loaded sample, the amount of spray solvent used, the applied spray voltage, the elution solvent, and the number of desalting cycles). To optimize the distance between the triangular-shaped paper and MS inlet, three different distances, 4, 8, and 12 mm were tested. It was found that the highest intensity of PFOA at m/z 412.9 was $3.77\text{E}8$ at 8 mm distance and ion signal decreased with increasing distance (Fig. S8a, Supporting Information). Thus, the distance between the paper and MS inlet was set to 8 mm for DPS-MS in this study. Sample loading volume onto paper substrate was examined. The sample was loaded from 4 to 10 μL and found highest intensity at 10 μL (Fig. S8b, Supporting Information, note that multiple drops of 10 μL of sample could further enhance ion signal as demonstrated below). The spray solvent volume effect was also examined for extraction and ionization of PFOA, and the highest intensity was found at 30 μL (shown in Fig. S8c). The highest ion signal was seen at -3.5 kV, as shown in Fig. S8d. To check the elution solvent effect, H_2O , ACN and MeOH were examined (Fig. S8e). The highest intensity was found for MeOH. Desalting cycle (10 μL H_2O was used each time) was checked and signal intensity was found to be the best after three times desalting for minimum signal suppression (shown in Fig. S8f). Finally, the optimized experimental conditions included: paper tip to MS inlet distance (8 mm); spray voltage (-3.5 kV), elution solvent (MeOH), sample loading volume (10 μL); spray solvent volume (30 μL MeOH), and desalting time (three times).

Signal stability was also checked for PFOA at m/z 412.9 in our DPS-MS experiment. After spraying the solvent of MeOH, there was a time delay of about 0.13 min to get a stable EIC current for m/z 412.9 (Fig. S9, Supporting Information). The delay might be caused by the electrophoretic migration of PFAS sample to the paper tip for spray. The signal stabilized for about 0.42 min (0.13–0.55 min) before declining.

3.2.2. Recovery test

To perform the recovery test, a 50 μM PFOA sample was prepared without using KCl (50 mM). This sample was tested first and 10 μL sample was directly spotted onto the triangular-shaped paper and eluted by MeOH for ionization. Another 50 μM PFOA sample was prepared in

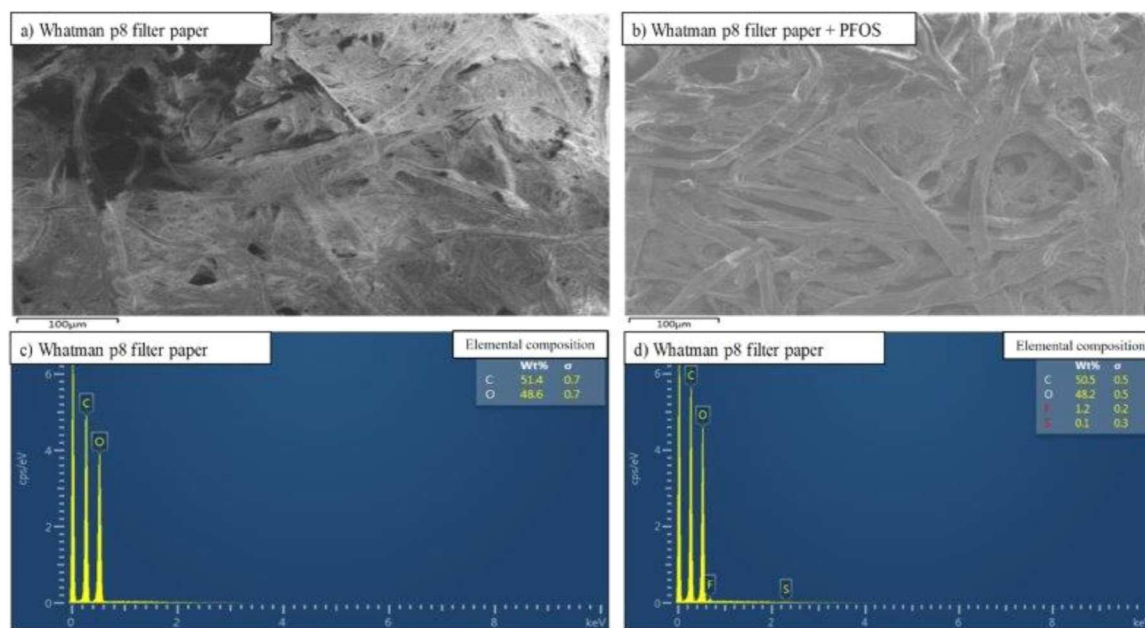


Fig. 4. SEM images of Whatman p8 filter paper a) before and b) after loading PFOS; EDX images of Whatman p8 filter paper c) before and d) after loading PFOS.

50 mM KCl for comparison. KCl matrix was removed from the PFOA sample by washing with 10 µL H₂O three times and then subjected to MS detection during DPS-MS analysis. Both samples were tested three times. Results were averaged and shown in Fig. S10 (Supporting Information). The intensity of PFOA without 50 mM KCl at m/z 412.9 was found 1.93E8. The signal intensity for PFOA with 50 mM KCl (washed with H₂O) was found 1.75E8. The signal ratio of two signal intensities was 91%, indicating the PFAS recovery of 91% after water washing for desalting. This result that PFOA does have strong interaction with the paper, which is in agreement with our assumption mentioned above.

3.2.3. PFOA analysis by DPS-MS vs. nanoESI-MS

After signal optimization, we conducted the analysis of PFOA, chosen as a test sample of PFAS, by DPS-MS compared to traditional nanoESI-MS. First, 50 µM PFOA in 50 mM KCl in H₂O was directly ionized by nanoESI, as shown in MS spectrum (Fig. 3a), an ion $C_7F_{15}COO^-$ at m/z 412.9 (measured m/z 412.96482, theoretical m/z 412.96643 and mass error: −3.9 ppm) corresponding to deprotonated PFOA, was detected but the intensity was low (7.88E4). The low intensity of PFOA ion was likely due to the ion suppression by the KCl salt matrix. By adding MeOH into the sample (final volume ratio of MeOH to H₂O: 1:1), the ion signal was improved to 2.04E6 (Fig. 3b). In contrast, when 50 µM PFOA aqueous solution containing 50 mM KCl was ionized by DPS-MS (via desalting on the paper using water, followed by MeOH elution for spray under high voltage), the PFOA signal was found to be 1.74E8, which was more than 80–2000 times higher than that from nanoESI-MS technique. Fig. S11 also shows the corresponding EIC spectra of the PFOA ion $[PFOA-H]^-$ (m/z 412.9) detected by nanoESI and DPS-MS, from which it can be seen that nanoESI ion signal was not very stable, probably due to the salt present in the samples. It can be seen that DPS-MS is advantageous over nanoESI for PFOA analysis in salt-containing samples, due to the capability to remove salt matrix.

In addition, DPS-MS is fast (about 3 min per sample), as desalting and spray ionization are performed using the same paper substrate. The assignment of the PFOA ion from DPS-MS was further confirmed through CID analysis. Upon CID, the ion at m/z 412.9 gave rise to fragment ions of m/z 368.9, 218.9, 168.9, and 118.9, by consecutive losses of CO₂ and C₃F₆, C₄F₈ or C₅F₁₀ (Fig. 3d) consistent with its structure.

3.2.4. Matrix test

In another set of experiments, we attempted to determine if the DPS-MS method could tolerate other salt matrices for detecting PFAS in a low concentration. In this test, we dissolved PFOA (1 nM) in 50 mM NaCl and 50 mM Na₂SO₄ and analyzed by DPS-MS. Again, the signal of PFOA at m/z 412.9 was clearly detected in the presence of both salts within mass error < 4 ppm (Fig. S12-b and S12-d). In contrast, nanoESI-MS failed to detect PFOA in the presence of salt NaCl or Na₂SO₄ (Fig. S12-a and S12-c).

3.2.5. Other PFASs analysis by DPS-MS

We further examined the application of DPS-MS to analyze other PFASs, including PFOS, PFHxA and PFBS (structures shown in Table 1). As shown in Fig. S13, 50 µM PFOS, PFHxA and PFBS in water containing 50 mM KCl were analyzed by DPS-MS and all these PFASs were clearly detected with high ion intensity (>10E8). Similar to the deprotonated PFOA (m/z 412.9), upon CID, these PFAS ions lose either CO₂ or SO₃ and undergo C-C bond cleavages by losses of C₂F₄, C₃F₆, etc. (Fig. S14 & Table 1), consistent with their ion assignments. This result demonstrated that DPS-MS is applicable to detecting PFAS in the presence of salt matrices in general.

3.3. Investigation of the interaction of PFAS with paper substrate

An effort was made to study the interaction of PFAS with the paper substrate used for DPS-MS. As mentioned above, PFAS molecule often contains a hydrophobic tail like perfluoroalkyl groups C_nF_{2n+1} and a hydrophilic polar head like CO₂ or SO₃. Due to possible polar-polar interaction between the polar head of targeted PFAS and cellulose of the paper substrate, PFAS would be retained on the paper when water is added onto the paper to wash away the salt matrix. To confirm the holding of PFAS on the surface of desalted paper, SEM and EDX investigation were conducted. SEM micrograph evidenced the fibrous nature of the surface with the presence of pores (Fig. 4a). The porous nature of the surface allowed the removal of salt by water rinsing. Upon spotting the PFOS on the surface, pores became smearing (Fig. 4b), suggesting the adsorption behavior of PFOS, or binding of PFOS with the filter paper surface. The EDX spectrum of this paper showed the existence of F and S peaks (Fig. 4d). Such EDX data confirmed the adsorption of PFOS on the paper substrate, as PFOS is the source for fluorine and sulfur. In

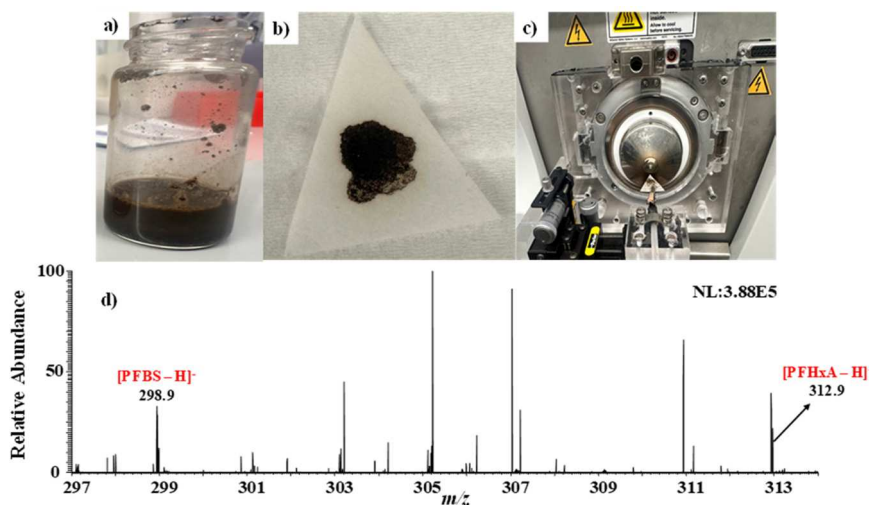


Fig. 5. Images showing a) soil extract with water, b) soil extract sample spotted onto the paper substrate; and c) DPS-MS apparatus. d) Negative ion mode DPS-MS spectrum of soil extract.

contrast, a blank paper only showed the elemental composition of paper consisting of C and O (Fig. 4c). Also, the relative elemental compositions of carbon and oxygen decreased following the adsorption of PFOS as shown in Figs. 4c and 4d. This result is in agreement with a study that was conducted to investigate the adsorption of PFAS on cellulose and modified cellulose [54]. It has been established that the sulfonic group of PFOS is negatively charged and hydrophilic. On the other hand, C-F chain of PFOS is more hydrophobic. Besides these polar-polar group interactions, the hydrophobicity of C-F enhanced intermolecular interaction of PFOS may also contribute to stabilizing PFOS adsorption onto the paper [33].

3.4. Sensitivity of DPS-MS for PFAS detection

In this study, we sought to evaluate the PFAS detection sensitivity of our DPS-MS method. For this experiment, we used samples containing a constant concentration of KCl (50 mM), while the concentration of PFOA, PFOS, PFHxA and PFBS was reduced from 50 μ M to 100 pM so that the KCl concentration was 5×10^8 times higher than PFAS. As shown in Fig. S15, all four PFAS ions were successfully detected (PFOA: measured m/z 412.96780, theoretical m/z 412.96643, mass error: 3.3 ppm; PFOS: measured m/z 498.93094, theoretical m/z 498.93022, mass error: 1.4 ppm; PFHxA: measured m/z 312.97278, theoretical m/z 312.97281, mass error: -0.1 ppm; PFBS: measured m/z 298.94292, theoretical m/z 298.94299, mass error: 0.2 ppm), despite the presence of a high concentration KCl matrix. In contrast, nanoESI-MS failed for such a detection (Figure not shown).

In the case of PFOA, we further lowered the PFOA concentration 10 times more to check the DPS-MS sensitivity. A 10 pM (4.1 ppt) PFOA sample in 50 mM KCl (KCl concentration was 5×10^9 times higher than PFOA) was prepared. In addition, a control experiment was also conducted in parallel by adding 50 mM KCl onto paper followed by paper washing, in which no PFOA was observed (Fig. S16a, Supporting Information). As shown in Fig. S16b (Supporting Information), the PFOA signal was clearly observed with good mass error (measured m/z 412.96770, theoretical m/z 412.96643, mass error: 2.4 ppm). Therefore, the DPS method appears to have a good desalting capability and, at the same time, high sensitivity for PFAS analysis.

3.4.1. Analysis of soil extract

We applied our DPS-MS method for PFAS analysis of soil sample extract. To conduct the experiment, 40 μ L soil sample extract (aqueous) was directly spotted onto paper and washed with 30 μ L water to clean up the background matrix. Moreover, a parallel experiment was conducted

by loading the same amount sample for PS-MS analysis without the desalting step. As shown in the corresponding spectra (Fig. S17), while PFBS at m/z 298.9 was detected in both cases with similar intensity, PFHxA m/z 312.9 was only detected by DPS with good mass accuracy (measured m/z 312.97170, theoretical m/z 312.97281, mass error: -3.5 ppm). The result suggests that background interference of the soil extract may have caused signal suppression in PS-MS, which could be removed by washing step during DPS-MS analysis. Initially detected PFAS was confirmed by collision-induced dissociation MS/MS study (shown in Fig. S18, note that, due to low intensity of PFHxA and PFBS, only one fragment ion was observed during CID event).

Quantitative analysis for DPS-MS analysis of PFAS is possible. Fig. 5 displays the images showing the viscous soil sample extract (Fig. 5a) and soil sample extract deposited on the paper substrate (Fig. 5b). Fig. 5c illustrates the DPS-MS apparatus where a three-axis XYZ platform [38] was used to support the paper substrate for position control, to gain signal stability and reproducibility for accurate quantitation. To run quantitative experiments, we doped PFOA as an internal standard (IS). Initially, a 40 μ L of soil sample extract (doped with a chosen internal standard (I.S.) of 400 pM PFOA) spotted onto the paper substrate and mass spectrum was acquired by DPS-MS, which showed the detection of PFBS (m/z 298.9) and PFHxA (m/z 312.9, Fig. 5d). To measure the amounts of PFBS and PFHxA in the soil extract sample, we made calibration curves of PFBS and PFHxA. As shown in Figs. S19 and 20, the plot was linear over PFBS and PFHxA concentrations ranging from (10 to 1000 pM) with a correlation coefficient higher than 0.99 (unweighted linear curve fitting was used for plotting). The excellent linearity of the plot indicated the DPS-MS method can be suitable for quantitative analysis. The limit of detection (LOD) for PFBS and PFHxA was calculated as 1.2 and 2.7 ppt, respectively. The amounts of PFBS and PFHxA in the soil extract was quantified and found to be 145.2 and 79.3 ppt, respectively. To achieve reproducible quantitative analysis results, we adopted paper substrates of the same size. We loaded the same volume (10 μ L) of sample onto the same location of the paper substrate each time. In addition, we fixed the paper substrate position (relative to MS inlet) using the xyz stage platform. We have also made a calibration curve of PFOA and PFOS at various concentrations and the LODs of PFOA and PFOS were found to be 1.9 and 4.5 ppt (Fig. S21 and 22, Supporting Information).

3.4.2. Direct soil sample analysis

In order to address the potential issue of PFAS dilution during the extraction process, we pursued an alternative approach by conducting direct analysis of solid soil samples without the need for extraction in

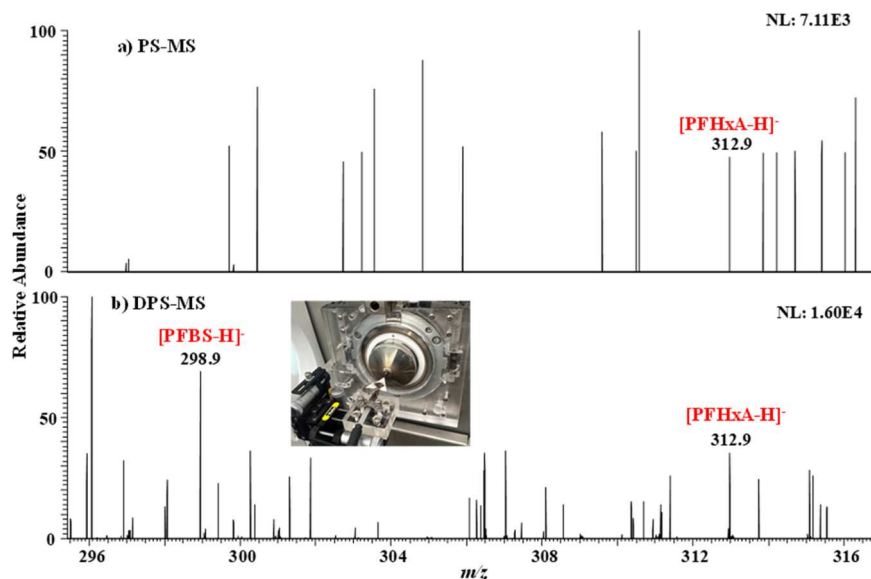


Fig. 6. Negative ion mode MS spectra of direct soil sample acquired by a) PS-MS (without water desalting) and b) DPS-MS (with water desalting).

DPS-MS analysis. This method would offer advantages such as time-saving and the use of a small amount of sample (e.g., 40 mg in this study). Typically, the detection of PFAS in soil samples involves labor-intensive sample preparation techniques that include solvent extraction followed by solid-phase extraction to concentrate PFAS. In our approach, we took a different route by directly applying a 40 mg soil sample onto a paper substrate. First, we applied PS-MS where we directly ionized the sample with MeOH (100%) was added to the soil sample for paper spray ionization with an applied high voltage of -3.5 kV. Fig. 6a shows detection of PFHxA with low signal intensity ($3.03E3$) which might be due to interference of background matrices. In contrast, by using DPS-MS (water was added to wash the soil sample and followed with spray ionization using MeOH and high voltage of -3.5 kV, both PFBS and PFHxA with elevated intensity ($1.14E4$ and $5.72E3$) were detected (Fig. 6b) by DPS-MS in which we washed the sample with H_2O and then ionized it using MeOH (100%). EIC spectra of the detected ions by PS-MS and DPS-MS are shown in Fig. S23. These strategies allowed us to streamline the analysis process and mitigate the challenges associated with matrix interference in soil samples when detecting PFAS. It can be seen that the desalting step in DPS-MS played a crucial role during soil analysis process as it would clean up background interference and boost up PFAS signal intensity.

4. Conclusions

This study shows the power of PS-MS and related DPS-MS for trace analysis of PFAS in different environmental samples. PS-MS integrates extraction and ionization together for sample analysis with minimum sample preparation, thus enabling a fast detection of PFAS in various water samples (1–2 min per sample). Remarkably, food packaging materials can be directly cut and analyzed with PS-MS. DPS-MS further integrates a desalting step together with extraction and ionization, using the same paper substrate, for analyzing samples with high background matrix. Our results showed that DPS-MS is able to detect trace amount of PFOA at 10 pM level in the presence of 50 mM of KCl and LODs for various PFAS is at low ppt level (1.2–4.5 ppt). The high tolerance of DPS-MS to salt allowed the fast analysis of PFAS in soil extract. More importantly, by using DPS-MS, a small amount of soil (e.g., 40 mg) can be directly analyzed within 3 min for PFAS detection without additional sample preparation. These results clearly suggest that PS-based MS techniques are fast, sensitive and versatile for PFAS analysis in water, food packaging and soil samples, which would find extensive real-world

applications in the fields of environmental, food, and health sciences.

Environmental implication

Per- and polyfluoroalkyl substances (PFAS) are omnipresent in environmental in trace level and poses crucial environmental issue. These compounds are linked to fetus development, suppressed vaccine response, affecting our immune systems. Trace detection of these compounds from complex samples is crucial for securing ecosystems and human health. Our manuscript reports a novel and unprecedented method, which is both fast (in few minutes per sample analysis) and sensitive (ppt level LOD), for trace detection and quantification of PFAS in various environmental samples including water, soil and food packaging material. Such a method would help find effective mitigation strategies to PFAS.

CRediT authorship contribution statement

Chen Hao: Conceptualization, Supervision. **Hassan Md. Tanim-Al:** Data curation, Formal analysis, Validation, Writing – original draft. **Sadik Omowunmi A.:** Formal analysis, Writing – review & editing. **Osonga Francis J.:** Formal analysis. **FNU Praneeth Ivan Joel:** Data curation. **Chen Xingzhi:** Data curation, Formal analysis. **Li Mengyan:** Formal analysis, Writing – review & editing.

Declaration of Generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author used ChatGPT from Chat.openai.com to paraphrase sentences to improve the language. After using this tool/service, the author reviewed and edited the content as needed and takes full responsibility for the content of the publication.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2023.133366](https://doi.org/10.1016/j.jhazmat.2023.133366).

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