Trends in Environmental Analytical Chemistry 37 (2023) e00198

Contents lists available at ScienceDirect

Trends in Environmental Analytical Chemistry

journal homepage: www.elsevier.com/locate/treac

Current and emerging analytical techniques for the determination of PFAS in environmental samples

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ARTICLE INFO

Keywords:
Per- and polyfluoroalkyl substances (PFAS)
Analysis
Sensors
Assays
Low cost detection

ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are a large group of synthetic chemicals used in many commercial products and applications such as polymers, fire-retarding foams, cookware and food packaging. PFAS pose significant threats to the environment and human health because of their high stability, potential toxicity and persistence in the environment. This review summarizes the status of analytical methods for detection of the broad spectrum of PFAS. Conventional analytical techniques are first described with focus on chromatographic/mass spectrometry methods, semi-quantitative approaches and passive samplers. Emerging colorimetric, spectrofluorometric and electrochemical methods, and field-deployable sensors are then reviewed, highlighting novel detection mechanisms, analytical performance and potential towards achieving low cost detection in environmental samples. Their low cost and portability can enable greater spatial and temporal data resolution and provide a more comprehensive characterization and screening of PFAS-containing samples, but require further development to reach detection at the regulatory permissible limits. Potential applications and a critical assessment of future needs and opportunities to translate these technologies into the field are discussed.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large group (>3000) of synthetic perfluorinated compounds ($C_nF_{2n+1}COOH$) widely used in many consumer products and industrial applications. Their characteristic structure consisting of several C–F bonds makes them highly stable and difficult to degrade by both environmental and metabolic processes, making them among the most environmentally persistent chemicals [1,2]. This inherent stability and resistance to water and oil have enabled broad implementation in a wide range of applications as a water repellent and for stain resistance in textiles, paints and personal care products, flame retardant foams, fluoropolymer additives and lubricants, and as water and grease-resistant food packaging [3]. Because of their wide use, PFAS have been detected in food, water, wastewater and human blood samples. Toxicological research has linked PFAS exposure with detrimental effects on organ systems, disruption of the development of the endocrine system, neurotoxicity and involvement in many diseases, including cancer [2,4–6]. Their persistence, high stability, toxicity and ability to bioaccumulate pose a significant threat to the environment and human health [7,8].

Due to toxicity concerns, these compounds are now enlisted as "persistent organic pollutants" by the Stockholm Convention (PFOS, PFOA, PFHxS and their salts) [9] and European Commission (PFOA, PFOS, PFNA, PFHxA) [10]. The Environmental Quality Standard (EQS) for the presence of PFOS traces in fresh and drinking water was set at a limit of $<$ 0.65 ppt in fresh water and 70 ppt in drinking water by the European commission and the U.S EPA [11]. The U.S EPA has issued interim health advisories for PFOA (0.004 ppt), PFOS (0.02 ppt), PFBS (2000 ppt) and GenX (10 ppt) [12]. The U.S EPA Method SW-846 test method 8324 is now standardized for 24 PFAS in non-portable water [13].

Many different sources of PFAS contribute to contamination, with the most common being wastewater treatment plants, military and firefighting training areas, industrial and consumer products discharges. Traces of PFAS, specifically perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are detected in surface water sediments, influent and effluents of wastewater treatment plants [14–16]. Varying PFAS, e.g. PFOA, PFNA (perfluorononanoic acid), PFDA (perfluorodecanoic acid), PFHxS (perfluorohexane sulfonate), and PFOS were detected in food through migration from microwavable containers and food contact papers [17,18]. Concentrations of PFOS in sewage and sewage treatment plants were found to be 20–190 ppt in samples from

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https://doi.org/10.1016/j.teac.2023.e00198
Received 29 August 2022; Received in revised form 4 February 2023; Accepted 7 February 2023
Available online 10 February 2023

the California Sewage Treatment Plant [19,20], ~449 ppt in raw sewage from cities in Germany [21] and 7.3–461.7 ppt in sewage treatment plant of Singapore [22]. The PFOS concentration in wastewater originating from a semiconductor manufacturing plant during the photolithographic process was 1650 ppm [23]. Food contamination from packaging materials is beginning to be investigated [24] and several agencies are looking to limit the use of long chain PFAS in food packaging [25]. The vast majority of contamination in the environment (~80%) was estimated to originate from fluoropolymers production and their use [26]. Given the extent of contamination, significant efforts are dedicated to develop methods to remove these chemicals from the environment [27]. The chemical stability, polarity and strong C-F bond energy make PFAS resistant to hydrolysis, photolysis and chemical degradation [28] and thus advanced oxidation and adsorption processes have so far been the most successful [27,29–34].

The EPA and several states have begun to require analysis of different PFAS in drinking water and other matrices to assure public health. Currently available methods to detect PFAS include gas or liquid chromatography (GC or LC) tandem mass spectrometry (MS/MS), methods that are expensive, time consuming and require samples to be sent to a centralized laboratory for analysis. While these methods are selective and sensitive, field analysis is limited due to lack of field-deployable techniques. Detection of PFAS is challenging because these compounds lack chromophores or electroactive groups and thus are not optical or electrochemically active. Therefore, methods such as UV-Vis spectroscopy or electrochemistry cannot be directly applied to measure these compounds. The low regulatory limits, e.g. 70 parts per trillion (70 ng/L or ppt) imposed by the EPA, or 10 ppt in some states [35] pose additional challenges for detection. Very recently, the US-EPA has released new guideline limits at levels as low as 0.004 ppt for PFOA in drinking water, posing significant challenges and increasing the need to develop ultrasensitive methods for detection [12]. The increased regulation [12,35] will involve a significant increase in testing; therefore, there is an urgent need to expand the arsenal of analytical methodologies with significantly higher sensitivity and lower cost than currently used methods. The development of low-cost field deployable tools and sensors that can identify and screen samples for PFAS is of particular interest [36]. If available, these could help to more rapidly assess presence, distribution and concentrations of PFAS and reduce analysis costs [37] before subjecting samples to the more complex LC-MS/MS.

This paper provides a critical overview of the state-of-the-art analytical methodologies for PFAS measurement, their development status, advantages and limitations. The importance of structures and the most commonly used methods to determine PFAS are briefly reviewed in the first part of the paper. In the second part, a discussion of emerging methods and tools is provided along with the detection mechanisms and examples of possible implementation for field measurements. Future technological development needs and implementation challenges, as well as adaptation of these tools to enable a more comprehensive characterization and screening of PFAS-containing samples is also highlighted.

2. Structural determinants of PFAS

The structural diversity of PFAS includes short and long chain compounds containing a fluorinated hydrophobic tail and a hydrophilic functional group [38]. Fig. 1 shows a selection of some of the most studied PFAS and the replacement Gen X (hexafluoropropylene Oxide (HFPO) dimer acid and its ammonium salt), which is believed to be less toxic and bioaccumulative than PFOA. Recent rodent studies have shown it is as toxic as PFOA [39]. A characteristic of PFAS is the perfluorocarbon moiety, which is responsible for the stability, persistence and non-degradability; these features earn these compounds the name "forever chemicals". In general, the environmental, health and regulatory communities have been interested in long chain perfluoroalkyl sulfonic acids ($C_nF_{2n+1}SO_3H$, $n \geq 6$, PFSAs) and perfluoroalkyl carboxylic acids ($C_nF_{2n+1}COOH$, $n \geq 7$, PFCAs) [40]. PFAS also exist as families of isomers due to branching of the C backbone.

Many PFAS are acids (e.g. carboxylic, sulfonic, sulfinic, phosphonic, and phosphinic acids) that can be protonated or neutralized, depending on the pH of the environment. Such forms are generally abbreviated as H-PFOS, PFOS, and (H-)PFOS for the protonated, anionic, and combined forms. Another category of fluorinated polymers, e.g., fluoropolymers (polytetrafluoroethylene (PTFE)), perfluoropolyether (PFPE) and side-chain fluorinated polymers (fluorinated acrylate), contain carbon-only or C and O polymer backbones with fluorine directly attached to carbon and molecular segments linked together versus non-polymers (perfluoroalkyl and polyfluoroalkyl) in which all H on the C backbone have been replaced by fluorine such as PFOA, PFNA, PFOS [40]. The chain length plays a significant role in the behavior of PFAS, their fate

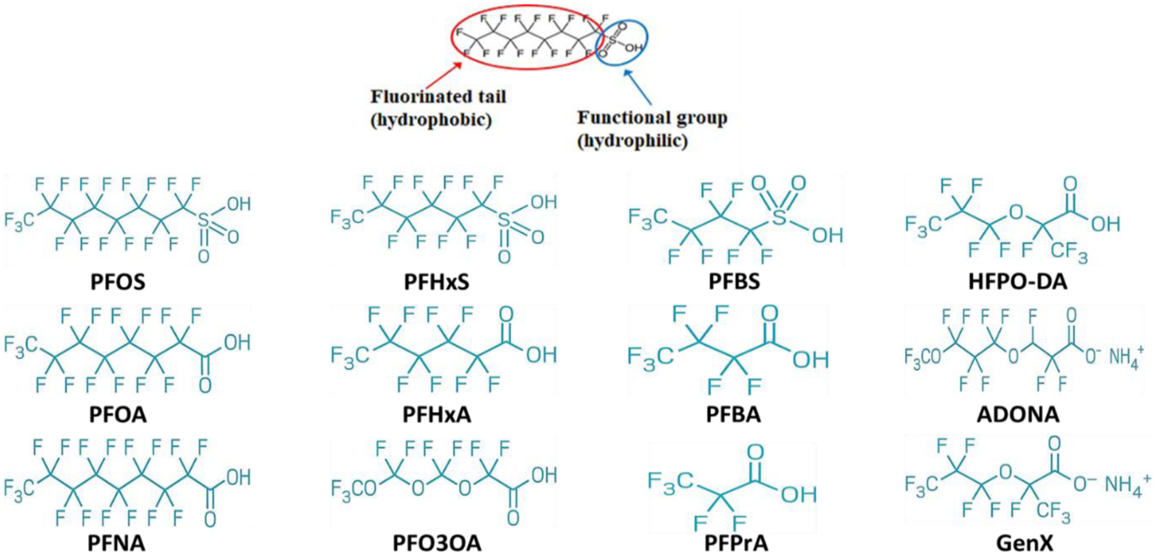

Fig. 1. Examples of chemical structures and structural determinants of common PFAS compounds. PFOS (Perfluorooctanesulfonic acid), PFHxS (Perfluorohexane sulfonic acid), PFBS (Perfluorobutanesulfonic acid), HFPO-DA (Hexafluoropropylene oxide dimer acid), PFOA (Perfluorooctanoic acid), PFHxA (Perfluorohexanoic acid), PFBA (Perfluorobutanoic acid), ADONA (3H-Perfluoro-3-[(3-methoxy-propoxy)propanoic acid], ammonium salt), PFNA (Perfluorononanoic acid), PFO3OA (Perfluoro-3,5,7-trioxaoctanoic acid), PFPrA (Perfluoropropanoic acid), (GenX; FRD-902).

and transport in the environment, as well as their measurements. The extent of fluorination and the location of the F atoms is also important. The longer chains have been the most used and studied for their properties, particularly the PFOS and PFOA. Due to the increased regulations and concerns over toxicity and long-term effects of long chain PFAS, shorter chains are considered by the manufacturing industry, but the health and environmental impacts of these shorter chains compounds are not well characterized [41]. Nevertheless, there is evidence to indicate that shorter chains are not the solution, but instead pose more problems. Shorter chain PFAS are highly mobile and can migrate from their sources though air and water, and be easily taken up by plants [42]. They are also more difficult to detect and remove from matrices, making their analysis and remediation more challenging.

3. Conventional methods for PFAS measurements

PFAS analysis is performed using traditional analytical instrumentation, in particular coupled chromatography with mass spectrometry LC-MS/MS [43]. This approach is selective and quantitative with detection limits in the low ppt range. Currently approved EPA methods involve the use of solid-phase extraction (SPE) to concentrate the sample followed by LC-MS/MS analysis. This method provides information regarding compound occurrence and concentrations based on multiple lines of evidence (i.e. retention time, precursor/product ion pairs) using reference standards. Currently, standards are available for < 100 of the thousands of potentially relevant PFAS [44]. Chromatography enables separation of the individual components in a mixture prior to MS detection and significantly enhances our ability to understand sample composition. The majority of PFAS listed by the EPA are detected by LC-MS [13,45,46]. However, there are several classes of neutral and volatile PFAS where gas chromatography is the preferred separation technique [47–49]. Beyond separation before entering the MS, the retention time in the chromatographic system is indicative of the individual component's physicochemical properties such as vapor pressure and octanol-water partitioning coefficients (K_{ow}). The retention time, log K_{ow} relationship of several homologous PFAS classes enables feature classification of these compounds [50]. Chromatographic behavior can supplement MS data when attempting to identify the molecular formula of an unknown feature. Newly identified PFAS can be compiled in a spectral library for application in future analyses. Prior work has identified a significant fraction of unidentified PFAS in AFFF [9,51,52], but additional compounds may still be present. Further, few studies have investigated unknown PFAS in non-AFFF sources [53].

Few laboratories have suitable instrumentation and expertise to perform PFAS analysis, so the cost per sample of ~ $200–300 makes such testing prohibitive for routine analysis. Given the interest in large scale monitoring of PFAS distribution and transport, it would be extremely valuable to be able to take samples from many locations simultaneously and analyze them in the field. Thus, more inexpensive sampling and monitoring tools are needed to provide an estimate of the overall distribution of PFAS and to assess treatment efficacy and potential exposure.

4. Passive sampling

Because the target PFAS concentration is extremely low and samples contain a variety of compounds, passive sampling approaches are used to concentrate the wide range of PFAS and create standardized procedures for field sampling and analysis. The use of passive sampling provides the necessary increase in sensitivity and selectivity. Most current analysis of PFAS is performed using passive sampling which allows the uptake and the desorption of the PFAS from the sampling media, and then analyzing the extract using chromatography coupled with MS methods [43]. In passive sampling, the analyte is collected from the sample through diffusion and partition in a collection medium [54] as governed by Fick's Law of Diffusion [55]. The uptake profile and sampling rate is determined from calibration studies and the analyte concentration is then measured at the end of the sampling period by correlation to a calibrated analyte concentration range in accordance to QC/QA procedures [54,56].

Most passive sampling methods for PFAS have been developed for ionizable PFAS (C5-C11). Passive sampling approaches include permeation devices, polyurethane foam (PUF) disks, solid phase microextraction fibers, diffusion gradient thin films (DGT) and thermal desorption tubes packed with sorbent materials [57–59]. The polar organic chemical integrative sampler (POCIS) has been the most commonly used sampler for ionizable PFAS [56]. Standard POCISs utilize a sorbent enclosed between polyethersulphone (PES) membranes including PUF foam, sorbent impregnated PUF or anion exchange sorbents (e.g. Strata XAW) to capture species that are ionized in aqueous solutions, but some conventional ion exchange sorbents are only applicable to a limited range of PFAS [58,60]. Kazerson et al. [60] modified a POCIS sampler with a commercially available weak anion exchange sorbent as a receiving phase placed between two poly-ethersulfone membranes for field detection of PFCA in a range of 0.1–15 ppt [60]. Kaserzon et al. [61] also developed a passive sampling device using microporous polyethylene (PE) tubes for the PFAS monitoring in groundwater. Seventeen PFAS were detected by using PE passive samplers. These sampler tubes were deployed by Gardiner et al. [62] at three different sites to test the surface water, showing a linear PFAS uptake over the 16–29 days. Becanova et al.[63] synthesized new graphene based hydrogels consisting of 4% porous graphene and 96% water, as new hybrid materials to pre-concentrate PFAS from ppt levels. Pristine graphene showed good uptake for long chain PFAS. The modified graphene monolith with diazonium-based chemistry showed to facilitate the uptake of short chain PFAS, and could potentially be used to pre-concentrate samples. Passive air samplers have been found suitable for measurements of PFAS in the atmosphere for several compounds: PFCA (perfluoroalkyl carboxylic acid), PFSA (perfluoroalkane sulfonic acids), FTOH (fluorotelomer alcohols), FTMAC (fluorotelomer methacrylate), FTAC (fluorotelomer acrylated), FOSA (perfluorooctane sulfonamides) and FOSE (perfluorooctane sulfonamidoethanol) [64], with detection in the ng per 46 m^3 of air. A thin film passive sampler based on a weak anion exchanger (WAX) showed the ability to monitor PFCA, PFSA, FTSA (fluorotelomer sulfonic acid) and GenX with a binding capacity of at least 440 mg PFAS per sampler and functionality of samples from wastewater treatment plants and rivers [59]. Recent innovations include the use of modified organosilica adsorbents cross-linked with an amine polymer (polyethylene amine, PEI) and Cu^{2+} to promote binding of short chain PFAS [65]. The Cu^{2+}-PEI helped maximize the hydrophobic and ion exchange interactions and create a higher affinity sorbent with the ability to reach a LOD$<$ 70 ppt. An increase of 500% in the sampling rate in perfluorobutyric acid (PFBA) was observed when Cu^{2+} was added to the resin. An overview of the calibration and application of passive sampling for PFAS analysis can be found in reference [56].

5. Semi-quantitative assays

Most environmental matrices contain traces of PFAS and their precursors, which makes the analysis of PFAS challenging. Analysis is even more difficult when the precursor structure and standards are not available. Semi-quantitative assays such as the total oxidizable precursors (TOP) and the total organic fluorine content (TOF) have been developed that take into account PFAS compounds and precursors of unknown structure, enabling a more complete analysis of PFAS contamination. These assays are particularly useful for those compounds that would otherwise be missed in conventional techniques, such as LC-MS/MS, which are not able to detect precursor compounds due to their unknown structures and unavailability of standards. TOP and TOF are also particularly useful to measure in situ precursor behavior.

5.1. Total oxidizable precursor (TOP)

The TOP assay allows for the investigation of PFAS precursors through their oxidative conversion into measurable perfluorinated alkyl acids (PFAAs), typically through the use of hydroxyl radicals [66]. During the degradation process, the radicals first attack the non C-F fragments, and then the C-F chains, leading to variations in the TOP assay products [67]. Fluorinated compounds such as PFSA, PFCA and PFAA formed during the decomposition of non-fluorinated parts of the precursor molecule can be determined by this assay. TOP enables detection of known and unknown precursors, replacing or complementing conventional analytical tools. The effectiveness of the TOP assay for the selective detection of PFAS from AFFF was studied and adapted to app-based smartphone quantification, demonstrating potential as a pre-screening tool for semi-quantitative detection [67]. The inclusion of short chains in the TOP molar balance also enables a more complete analysis of PFAS contamination.

5.1.1. Total organic fluorine (TOF)

The TOF method provides concentration of total fluorine, and is typically used to measures the total PFAS using various approaches: i) particle induced gamma ray emission, ii) combustion ion chromatography and iii) absorbable organic fluorine. Other methods are based on fluorine-19 nuclear magnetic resonance spectroscopy (19F NMR), inductively coupled plasma/mass spectrometry (ICP-MS/MS) and vacuum ultraviolet (VUV) photolysis. A report detailing a study of absorbable organically bound fluorine (AOF) and organic bound halogens in environmental samples measured AOF values of 555 ppb in industrial wastewaters by combustion ion chromatography. This value is 273-times higher than the total of individual PFAS, calculated as F measured with HPLC-MS/MS [68]. TOF and extractable fluorine methods were critically reviewed by Schultes et al. with an application for measurement in food packaging, highlighting advantages and inconsistencies among different methods, along with their performances [69].

6. Emerging low cost detection methods

While conventional chromatographic methods provide the required sensitivity and selectivity for analysis, the complex analysis procedure, need for specialized equipment and trained personnel, and the high cost per sample ($200–300) significantly hinders the available testing capabilities. The 2019 EPA PFAS Action Plan [70] identified the need for new analytical methods and tools for monitoring PFAS in order to more comprehensively assess the distribution, impact and concentrations of these chemicals. Low cost field-deployable methods, if available, can be used by communities, industries and organizations to assess PFAS in drinking water and waste streams, and assist with remediation efforts in critical areas of PFAS contamination. Such methods might not necessarily replace the conventional LC or GC-MS/MS procedures, or the semi-quantitative assays, but can provide a screening tool to complement analysis and facilitate testing of a larger number of samples.

The characteristics of an “ideal” low-cost method for monitoring PFAS in the field are: i) compact, portable and inexpensive; ii) sensitive to the level of contamination down to the ppt-level regulatory limits and performing according to QC/QA procedures; iii) uses low cost equipment and power supply; iv) operable at the point of source; v) simple to use with a user-friendly interface, and vi) can be additively manufactured for large scale use. Because PFAS are not optically or electrochemically active, they cannot be directly measured by low cost spectroscopic or electrochemical methods. Therefore, most procedures involve indirect methods based on redox reporters or specifically engineered interfaces, such as molecularly imprinted polymers (MIPs) that are able to bind and recognize PFAS. Fig. 2 summarizes the different approaches for low-cost PFAS detection. The following section provides an overview of recently reported low-cost detection methods for PFAS, focusing on spectroscopic and electrochemical procedures, their detection mechanism and performance characteristics.

6.1. Optical assays and sensors

6.1.1. Colorimetric assays

Colorimetric assays have gained interest for chemical analysis because of their simplicity in operation making them amenable to non-expert use, their fast response time and the low-cost of instrumentation. Colorimetric methods for PFAS detection are typically based on two principles: 1) changes in spectral features of colloidal nanoparticles (NPs) upon interaction with PFAS, or PFAS-induced aggregation, and 2) changes in UV-Vis spectra of redox dyes upon PFAS binding. Most reported colorimetric strategies involve the use of gold (Au)NPs with measurements of changes in their surface properties and aggregation status upon interaction with PFAS [71,72]. Nano-enabled detection with nano-based receptors and amplifiers based on the surface interaction between NPs and PFAS have potential for low cost sensing of PFAS [73]. The detection limits of these methods are in general in the ppb (μg/L), several orders of magnitude higher than the regulatory permissible

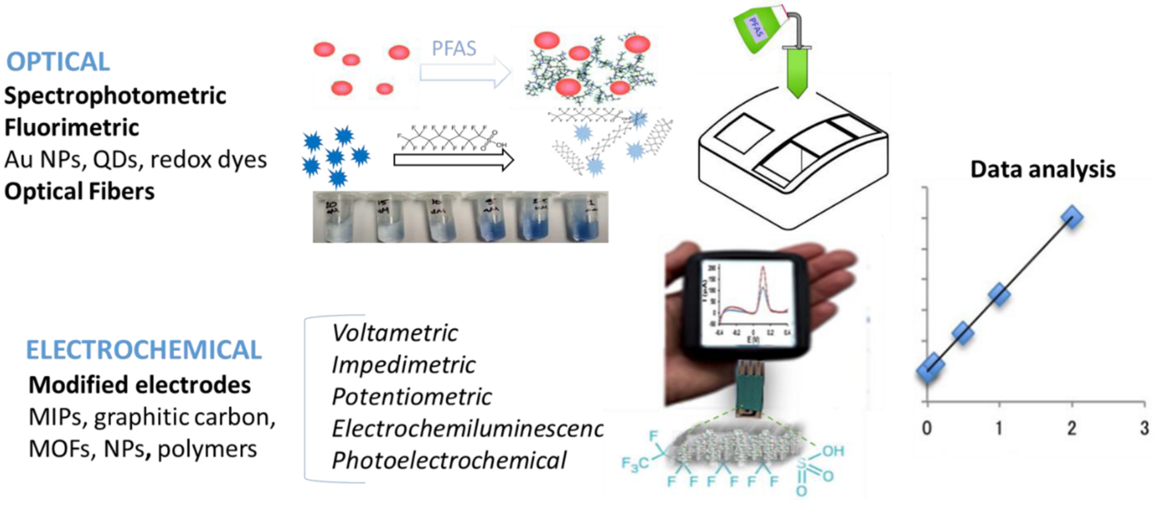

Fig. 2. Optical and electrochemical procedures for low cost detection of PFAS summarizing the different spectroscopic, fluorimetric and optical fibers with optical detection, and electrochemical methods with chemically modified electrodes based on MIPs, graphitic carbon, polymers, nanoparticles (NPs) or metal organic framework (MOFs).

limits, making them of limited use for measurement of PFAS in environmental settings. An assay using AuNPs modified with thiol-terminated polystyrene reported a detection limit (*LOD*) for PFOA of 103 ppm [74] and 10 ppb when the AuNPs were modified with poly (ethylene glycol) and perfluoroalkyl thiols (Au@PEG-F NPs) [75]. The adsorption of PFOS on Au@PEG-F NPs was due to the F-F interactions induced by the F-thiols [75], leading to accumulation of Au@PEG-F NPs, which induces the probe to precipitate resulting in a concentration dependent change in the absorbance of the AuNPs (Fig. 3**A**). The detection limit with this colorimetric probe sensing is ~ 10 ppb with good linear range. This assay shows potential for low-cost detection of PFAS [75], but requires significant improvements in sensitivity to be used in the field. Recently, a nanoelectrochemistry-based approach using AgNPs as redox probes for PFAS was reported which enables ultrasensitive monitoring of the interaction of PFOS at the surface of single AgNPs, enabling monitoring of single particle events involving PFOS down to ppt concentrations [76].

A second category of colorimetric approaches involves the use of redox dyes such as methylene blue (MB) [77] and methylene green (MG) [78] that bind PFAS through ion pairing, changing the intensity of their UV-Vis response in a concentration-dependent manner. Anionic surfactants like PFOA and PFOS interact with cationic dyes such as MB, MG or ethyl violet and form an ion pair at the PFAS hydrophobic end. The MB assay was adapted to smartphone-based color measurements with the capability to perform analysis within 5 min, suggesting that this assay has potential as a pre-screening tool for on-site analysis. The assay was interfaced with SPE to pre-concentrate the sample and improve sensitivity. LOD of 0.5 ppb and a linearity range between 10 and 1000 ppb were reported. Using the same principle but with MG dye, the colorimetric assay was adapted to a paper based analytical device (PAD) for PFOS [78]. A detection limit of 10 ppm was reported, but visual color changes can be seen only for very high concentrations of PFOS (>50 ppm). The method has shown significant cross reactivity from heavy metals, as well as other anions, cations and surfactants. The lack of selectivity and the high LOD (10 ppm), far from the low ppt/ppq advisory limits set by the EPA, makes this assay unsuited for field analysis. Nevertheless, the low cost of the assay (~1$) and short analysis time (<15 min) makes it an interesting candidate for further development. A colorimetric assay based on the use of a porphyrin receptor that has the capability to bind PFOA was reported as a rapid colorimetric test with spectroscopic analysis [79]. Porphyrins are known receptor molecules and ideal candidates for molecular sensing due to their strong absorbance and potential to be functionalized in order to achieve selectivity towards a target. The method showed PFOA detection capabilities in the concentration range 1–16 ppm and enabled measurements in soil extractions [79].

6.1.2. *Fluorescent and luminescence detection*

Fluorimetric assays for PFAS are based on measurements of the fluorescent signal of common fluorophores in solution or immobilized on solid platforms before and after interaction with PFAS. An interesting approach is to combine fluorescent dyes with molecularly imprinted polymers (MIP) using MIP-grafted on SiO_2 NPs as shown in Fig. 3C [80]. Molecular imprinting is typically used to prepare polymeric materials with specific molecular recognition receptor cages with high affinity for a specific target. A unique feature of MIPs is that they enable detection of non-electroactive molecules such as the class of PFAS. To construct a MIP-based fluorescent assay for PFAS, a MIP fluorescence reporter was first synthesized by grafting a MIP and the dye onto the surface of SiO_2 NPs to produce dye-(NH_2)-SiO_2 NPs. Fluorescein 6-isothiocyanate (FTC) fluorophore and amine ligands served as receptor sites for PFAS binding and binding occurred through hydrogen interactions and acid-base pairing [80]. The binding of PFOS to the dye-SiO_2 induces fluorescence quenching due to changes in the electron transfer of the dye at the surface of the SiO_2. The method's sensitivity is down to 5.57 ppb with a linearity range from 5.57 to 48.5 ppb. Polymeric sorbents can be synthesized and are amenable to molecular imprinting using a fluorous monomer and cross-linker and can be designed to recognize PFAS compounds via hydrogen bonding and F-F interaction [81]. Other strategies involve the use of CdS quantum dots (QD) with quantification of the fluorescence quenching induced by PFOA as shown in Fig. 3B [82]. The quenching mechanism was explained by the interaction between the anionic carboxylate groups of CdQD and PFOA changing the surface charge thus inducing aggregation via F-F affinity interactions.

A fluorescent indicator replacement assay developed via supramolecular assembly of guanidinocalix[5]arene on iron oxide NPs was reported for combined fluorescent detection and removal [83]. Two calixarenes, guanidinocalix[5]arene (GC5A-6C and GC5A-12C) were

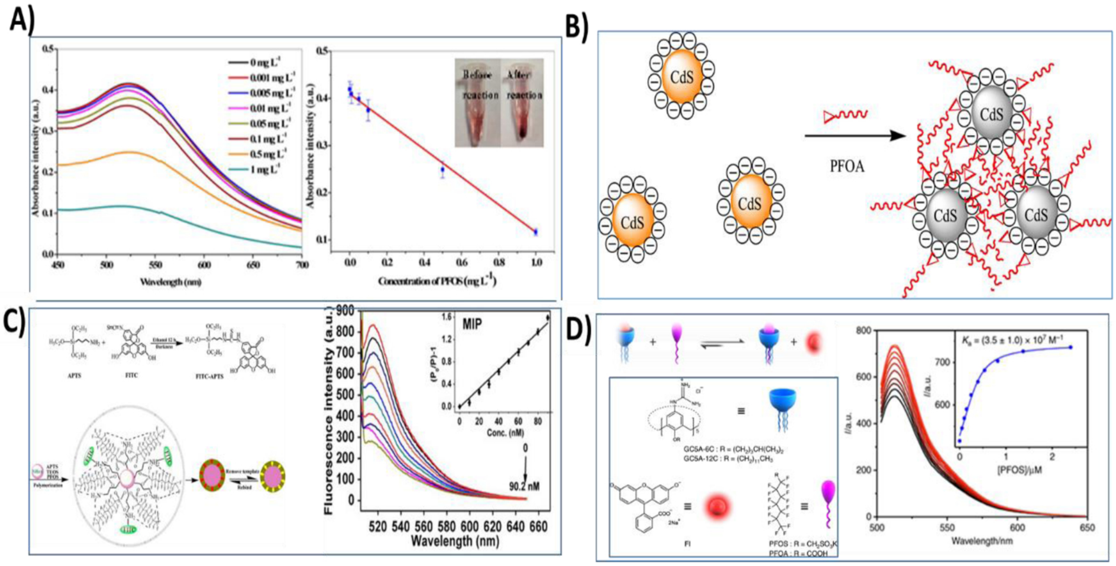

Fig. 3. Summary of spectroscopic and fluorescence based approaches for PFAS detection: (A) AuNPs-based assay using absorbance measurements of Au@PEG-F NPs in response to different concentrations of PFOS with corresponding calibration curve [75]. (B) QD-based fluorescence quenching of PFOA (with permission from Ref [82]). (C) Example of fluorometric detection using MIP-grafted on SiO_2 NPs showing synthesis procedure and spectra of MIP-capped FITC-APTS-SiO_2 NPs (40 ppb) with addition of different PFAS concentrations (with permission from Ref [80]). (D) Calixarene based fluorescence detection showing detection mechanism, chemical structures, and corresponding calibration curves for PFOS using the guanidinocalix[5]arene receptor (with permission from Ref [83]).

used as molecular receptors due to their ability to selectively bind to PFOS and PFOA targets, while iron oxide NPs were used to facilitate adsorption of PFOS/PFOA and for magnetic separation. The chemical structures, detection mechanism and the corresponding calibration curve for PFOS are summarized in Fig. 3**D**. Binding affinities of 3.5 $\pm$ 1.0 $\times$ 10^7 M^{-1} for PFOS and 1.7 $\pm$ 0.3 $\times$ 10^7 M^{-1} for PFOA were reported using the GC5A-6C receptor, with LODs of 11.3 $\pm$ 0.2 ppb and 10.9 $\pm$ 0.1 ppb for PFOS and PFOA, respectively. The assay was selective for PFOS and PFOA, and showed negligible responses to CTAB, octanosulfonic acid, perfluorohexane, NaCl, Na_2SO_4, KCL and $MgCl_2$. The ability of these receptors to bind selectively to PFAS opens up opportunities for designing fluorescent-based analytical assays and sensors, but the sensitivity of the method still needs significant improvement to meet the requirements for real world applications.

A switchable turn on/turn off sensor to detect PFOA was recently developed using a luminescent metal-organic framework prepared using a chromophore ligand 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine (H_4tcpp) [84]. The luminescent MOF showed sensitivity and selectivity for turn-on detection of F^- and PFOA, with LODs of 1.3 ppb and 19 ppb for F^- and PFOA, respectively. The mechanism responsible for F binding was attributed to the acid–base interaction between the PFOA and the tcpp network. The interaction between F occurring primarily at the bridging -OH^- and the presence of N in the organic component. These studies suggest that synthetic design may be used to fabricate optically active molecules that have the ability to selectively bind and detect PFAS for high performance sensors.

6.2. *Electrochemical methods*

Electrochemical methods and sensors are recognized for their low cost, portability and sensitivity with on-site deployment capabilities [85]. Because PFAS are not electrochemically active, redox materials are typically used as a sensing probe to monitor changes in the electron transfer resistance upon PFAS binding. Few examples of low-cost electrochemical approaches for PFAS detection have been reported, most of them utilizing MIPs as synthetic receptors to cage PFAS at the surface of the working electrode. MIP-based electrochemical sensors are prepared by electropolymerization of a monomer in the presence of a cross-linking agent and the target, in this care a specific PFAS, which results in creation of molecular recognition sites that match the target molecule in shape and size [86]. In most cases, detection is accomplished by redox probes such as ferrocene carboxylic acids in solution. MIP-based electropolymerization enables the synthesis of polymeric sorbents with cavities that are selective for PFAS. A general imprinting process involves: i) mixing of template molecules with a fluorous monomer and a cross-linker polymerized to form a polymer network with the immobilized target, ii) extraction of the target, iii) binding of a complementary target (e.g. the analyte) into the cavity. These cavities should in principle have characteristics (size, charge and binding interactions) that are complementary to the target. A fluorous receptor MIP using 2,2,3,3,4,4-hexafluoropentan-1,5-diyl dimethacrylate (HFPDMA) as a cross linker showed that higher content of fluorine significantly increases the adsorption and retention of PFOA, via F-F interaction and hydrogen binding [81]. A PFOA-selective MIP was created using methacrylic acid (MA), a monomer and 2,2,3,4,4,-hexafluoropentan-1–5-diyl dimethacrylate (HFPDMA) which provides binding with the carboxylic group of the PFOA. Using this procedure, selectivity can be tailored to other PFAS such as PFOS by using 2-(dimethylamino)ethyl methacrylate, which promotes electrostatic binding with the sulfonate group of the PFOS. These MIPs can be used as materials for SPE extraction and as sensing probes for PFAS detection. A chemically modified MIP-coated electrode prepared using poly(*o*-phenylenediamine) (o-PD) and ferrocene carboxylic acid (FcCOOH) as redox probe enabled sensitive detection of PFOS with a LOD of 20 ppt [87,88]. The MIP cavities were created by electropolymerization of o-PD on flat gold electrodes and the electrochemical signal was generated by monitoring the signal of the FcCOOH probe using differential pulse voltammetry (DPV) [87] (Fig. 4**A)**. Using the same strategy, Dick et al. explored the surface chemistry of these MIPs and their selectivity and found adsorption of species such as humic acid and chloride on the electrode surface interfering with measurements [88], highlighting the lack of selectivity for these sensors.

The selectivity of MIPs towards specific PFAS could be improved by carefully choosing the structure and configuration of the monomer. Increased selectivity was achieved [89] using cationic functional monomer 4-vinylpyridine (4-Vpy) as a template for the adsorption of PFOS, due to the electrostatic interaction between the template and the monomer. The adsorption was pH dependent, and the platform showed reduced selectivity for high concentrations of PFOS due to charged particle buildup and double layer adsorption. The MIP [90] was further modified with chitosan and used as a sorption medium to remove PFOS from water. A review of the adsorption behavior of perfluorinated compounds on varying adsorbents can be found in reference [91]. Cao et al. [92] used binary functional monomers 4-vinyl pyridine (4-Vpy) and 2-trifluoromethyl acrylic acid (TFMAA), azobisisobutyronitrile (AIBN) as an initiator for the recognition of PFOA and PFOS in aqueous solutions, showing adsorption capacities of 6270 and 6420 ppm (mg kg^{-1}) for PFOS and PFOA respectively. The adsorption capacities are higher and do not change in acidic pH from 2 to 5 but decrease for pH higher than 5. The decrease in adsorption is due to change in the ionization state of some PFAS in the neutral to basic pH range. MIPs can also be prepared within multi-walled carbon nanotubes (MWCNTs) structures, which increases binding capacity for PFOA with a reported value of 12400 ppm (mg kg^{-1}) removal [93]. These platforms could be good candidates to improve selectivity and sensitivity of electrochemical sensors for PFAS.

Other detection strategies involve the use of metal organic framework (MOF)-modified microelectrode (ME)[94] with impedimetric detection and the monitoring of PFOS-induced bubble-nucleation of the hydrogen evolution reaction at a Pt ME [95]. The MOF-based design relies on the use of a mesoporous MOF, Cr-MIL-101 that has affinity for the fluorinated chains and the sulfonate group of the PFOS. PFOS was quantified by measuring the increase in impedance upon PFOS binding. A LOD of 0.5 ppt was reported [94]. Other detection modalities such as electrochemiluminescence (ECL) have also been used to measure PFOA on MIP-based sensors [96]. The electrode was prepared by electrochemically imprinting ultrathin graphitic carbon nitrides (g-C_3N_4) nanosheets within pyrrole using cyclic voltammetry and using PFOA as template. The g-C_3N_4 sheets with molecular imprinting (MIP@utg-C_3N_4) showed good stability and amplification of the ECL signal. The sensor had two linear ranges of concentration, 0.02–40 ppb and 50–400 ppb and a LOD of 0.01 ppb [96].

In addition to the above-mentioned methods, photoelectrochemistry (PEC) was also used as a detection technique with potential to increase sensitivity and miniaturization [97]. The method coupled photo-irradiation with electrochemical detection, taking advantage of the properties of both optical and electrochemical methods. TiO_2 NPs or other semiconducting metal oxides are generally used as photosensitizers for photocurrent conversion. Several studies have explored the use of PEC in conjunction with MIP for PFOSF analysis. A PEC sensor modified with a TiO_2 nanotube array and molecularly imprinted acrylamide was developed for detecting PFOS in the concentration range of 0.25–5 ppm with a LOD of 86ppb (S/N = 3) [32]. The imprinted acrylamide enhanced both the selectivity through the cage confinement effect and the photocurrent generation due to its electron transfer capability. In another work, bismuth oxyiodide (BiOI) nanoflakes arrays were used as electrode material to create a disposable sensing strip prepared by electrodeposition of the BiOI on a screen-printed electrode followed by grafting of a acrylamide-based MIP containing PFOSF as a template molecule (Fig. 4**B)** [98]. Upon template removal and target binding, the specific recognition and steric hindrance was due to PFOS binding. This induced a change in the charge transfer of electron donors

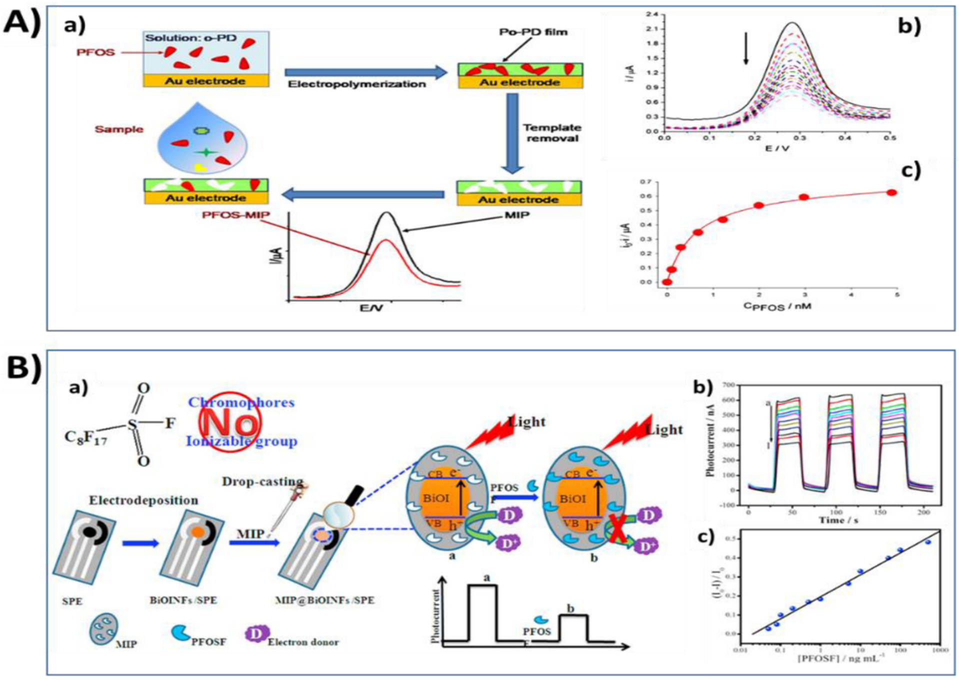

Fig. 4. Examples of electrochemical and photoelectrochemical detection showing: A) Fabrication of MIP-based sensor via electropolymerization of o-PD (a), measurement strategy for PFOS DPV signal (b) and calibration curve (c) of FcCOOH probe upon addition of varying PFOS concentrations (with permission from Refs [87]), and B) Schematic of the MIP@BiOINFs/SPE for the detection of PFOSF (a), photocurrent generation (b) and calibration curve (c) (reproduced with permission from Ref [98]).

at the electrode surface, further generating a concentration-dependent photocurrent decrease. This portable sensor showed a linear response in concentrations ranging from 0.05 to 500 ppb and a LOD of 0.01 ppb. A similar approach was reported by Gong et al. [99] who used AgI-BiOI nanoflake arrays to detect PFOA under the visible light irradiation, with a linear range 0.02–1000 ppb and a LOD of 0.01 ppb [99]. Photoelectrochemical detection can be potentially coupled with photodegradation [100] to create an integrated PFAS detection/destruction system with photocatalysts such as TiO_2 to photocatalytically degrade and photoelectrochemically detect PFAS.

To summarize, in the current development stage, emerging low-cost approaches suffer from limited sensitivity and lack of selectivity against co-existing species, ions or humic acid components. Table 1 provides a summary of the different colorimetric and electrochemical techniques used for the detection of PFAS with their detection principle and reported sensitivity.

7. Conclusions and recommendations for future research

The presence of PFAS in the environment and their risks to the environment and human health are well documented. While evidence highlighting the environmental health and safety concerns are increasing, the availability of analytical methods and instrumentation that can rapidly assess PFAS exposure in the field is limited. This review outlined the status of analytical methods covering both classical, e.g. LC-MS/MS, semi-quantitative and passive sampling, as well as emerging approaches with colorimetric, spectrofluorimetric and electrochemical detection. Table 2 provides a summary of the main methods for PFAS detection and analysis with their strengths and limitations. Conventional methods are expensive and not broadly available while the emerging low-cost methods lack sensitivity by several orders of magnitude and are unable to meet regulatory detection limits (e.g. 0.004 ppt PFOA). The development of low-cost sensors can help identify and prioritize samples for PFAS analysis and rapid intervention. Low cost portable methods that can be deployed remotely to measure individual or total PFAS would be highly valuable for quantification of PFAS contamination in situ [101]. However, despite their potential, existing sensors are not validated, and their performance including quality control/quality assurance (QC/QA) criteria and functionality in field conditions has not been demonstrated.

Because PFAS are not optically or electrochemically active, detection by low cost optical or electrochemical methods is significantly hindered. Different approaches that take advantage of the interaction of PFAS with redox active molecules and the development of molecular receptors for PFAS have been reported in an attempt to achieve the selectivity and sensitivity needed for detection. The colorimetric approaches are simple to use and inexpensive but they are not sufficiently selective, and with LOD limits in the ppm range, they lack sensitivity by several orders of magnitude compared to regulatory limits (ultralow ppt, e.g. 0.004 ppt for PFOA). Electrochemical sensors are portable and more sensitive than colorimetric approaches. Most reported electrochemical sensors use MIPs as recognition platform and LOD are typically in the low ppb,

Table 1
Examples of parameters and detection limits for different low cost detection techniques for PFAS analysis.

PFAS	Detection techniques	Detection mechanism	Concentration range	Limit of detection	Ref.
PFOS	Colorimetry	Au@PEG-F	1 ppb-1 ppm	10 ppb	[75]
PFOA, PFOS	Colorimetry	Methylene Blue	10–1000 ppb	0.5 ppb	[77]
PFOS	Paper-based analytical device	Methylene Green	1–500 ppm	10 ppm	[78]
PFOA	Fluorescence	CdS quantum dots	200 ppb-16 ppm	124 ppb	[82]
PFOS, PFOA	Fluorescence	guanidinocalix[5]arene	0–300 ppb	11 ppb	[83]
PFOA	luminescent	Metal–organic framework	0–80 ppm	19 ppb	[84]
PFOS	Differential Pulse Voltammetry	Molecularly imprinted polymer (MIP)	50 ppt - 750 ppb	20 ppt	[87]
PFOS	Impedimetric	Metal-organic framework (MOF) - interdigitated microelectrode (IDμE)	0.5 ppt – 1 ppb	0.5 ppt	[94]

Table 2
Summary of analytical methods for measurement of PFAS in environmental samples with their strengths and limitations.

Method	Strengths	Limitations
Coupled chromatography with mass spectrometry (LC-MS/MS)	Selective and quantitative Low detection limits in the low ppt range (or lower when used in conjunction with SPE) Effective providing Established and validated methods (SW-846 test method 8324).	High cost per sample (>200 $) Limited instrumentation available Lengthy and complex analysis procedure Requires expertise and skilled personnel Cost prohibitive for routine analysis PFAS precursors are not detected
Semi-quantitative assays: Total oxidizable precursors (TOP) Total organic fluorine (TOF)	Enable measurements of PFAS precursors Can be used as a pre-screening tool Provides a more complete analysis of PFAS, including short chain and oxidizable precursors	Limited sensitivity and selectivity Require expertise and skilled personnel
Optical assays and sensors	Inexpensive, easy-to-use and fast Instrumentation broadly available; can be adapted to smart-phone based detection Can be miniaturized and used in the field Could provide a ‘total PFAS content’	Indirect quantification with the use of redox dyes or NP indicators Detection limits in the ppm or ppb range; does not meet regulatory permissible limits Interferences from coexisting species Need performance validation and QC/QA
Electrochemical assays and sensors; with NPs, organic dyes, MIPs based detection	Inexpensive, easy-to-use and fast Low-cost instrumentation available Can be deployed in the field Could provide a ‘total PFAS content’	Indirect quantification through the use of redox indicators Detection limits in the ppb range; does not meet regulatory permissible limits Interferences from coexisting species Need performance validation and QC/QA

rarely achieving high ppt levels. Moreover, some studies have shown that MIPs suffer from selectivity with strong interferences from other species such as humic acid and other coexisting anions [88]. Potentially, these can be interfaced with extraction systems, such as SPE cartridges to remove pre-concentrate the sample and increase sensitivity.

Key fundamental needs remain to enable the development of field-deployable methods for PFAS analysis particularly with respect to: 1) the development of new materials and molecular receptors that have the capability to selectively bind an individual or a class of PFAS (e.g. short vs long chain); 2) detection modalities and mechanisms to amplify optical and electrochemical signals in order to achieve the low detection limits imposed by regulatory agencies (e.g. ultralow ng/L or ppt); 3) validation, standardization, and translation of the technology for an expanding range of PFAS. At the present time, the interaction of PFAS with different types of materials is largely unknown, which limits the capability to innovative in this field. While it is generally known that electrostatic and hydrophobic interactions contribute to PFAS adsorption, less is known about the effect of surface chemistry, composition, geometry and molecular arrangement. Fundamental work in the synthesis and supramolecular assembly of novel materials and complexes with specific binding sites for PFAS is essential to the development of these methods.

A mechanistic understanding of the interactions of PFAS with varying surfaces, at macro and nanoscale levels is thus a critical next step to identify key parameters (surface charge, surface functional groups and molecular arrangement) and design surfaces for analytical method development. Furthermore, determination of analytical performance and figures of merit in real samples, in addition to validation and standardization are needed to ensure that these methods are suitable for field deployment. Additionally, inter-laboratory validation, performance evaluation and QC/QA criteria, and the manufacturing of these platforms for large-scale use, and demonstration of robustness and functionality in the field will be critical to advancing adoption and implementation of these methods by industry and regulatory agencies. Eventually, these could be integrated in an analytical workflow [102] and be used alone or in conjunction with other methods and sample collection/extraction/purification kits for measurements of individual or subgroups of PFAS families across different types of matrices. Spectroscopic and electrochemical methods have potential as low cost easy-to-use platforms for PFAS. However, significant developments of new materials and detection modalities are needed to advance their capabilities for field deployment, validation and standardization. These advanced methods are a needed and important development step to assists researchers and the community in more effectively measuring and assessing PFAS contamination.

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

No data was used for the research described in the article.

Acknowledgements

This work was funded by the National Science Foundation under Grant No. 2141017. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation. The authors also thank the NYS Center of Excellence in Healthy Water Solutions for sponsoring an academic-industry exploratory workshop focusing on PFAS analysis. Abd Ur Rehman gratefully acknowledge the Higher Education Commission (HEC) of Pakistan.

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