



Recent advances in the analysis of per- and polyfluoroalkyl substances (PFAS)—A review

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS), that are widely used in different industrial and commercial activities, have become emerging contaminants of concern. Thus, the evaluation of PFAS presence in diverse environmental matrices is of paramount importance, leading to the necessity in development of different types of analytical methods to analyse the trace amounts of PFAS with varying selectivity and sensitivity. Analytical methods that have been advanced and employed for PFAS identification are critically described with their strengths, limitations and future potentials in this review. This review includes, (i) instrument analytical methodologies, mainly focusing on sample preparation, extraction and recovery analysis, (ii) nanoparticle-based sensors, and an app-based smartphone portable sensor, for the monitoring and sensing of PFAS in different environmental matrices. Furthermore, (iii) total oxidisable precursor assay (TOPA), content of total organic fluorine (TOF) as well as total fluorine (TF) are also reviewed, which provide fundamental tools towards achieving precursor quantification and closing mass balance analysis.

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Contents

1. Introduction.....	2
1.1. PFAS.....	2
1.2. Classification of PFAS	2
2. Chromatography techniques for PFAS analysis.....	2
2.1. Liquid chromatography (LC).....	7
2.1.1. Analysis of PFAS in solid matrices	8
2.1.2. Analysis of PFAS in aqueous matrices	9
2.1.3. Analysis of PFAS in food matrices.....	10
2.1.4. Analysis of PFAS in biological matrices.....	11
2.1.5. Analysis of PFAS in air, dust and other	11
2.2. Gas chromatography (GC).....	12
3. Sensors for PFAS detection.....	12

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3.1. Nanoparticle-based sensor.....	12
3.2. Smartphone app-based sensor.....	14
4. TOPA and TOF for PFAS and precursors analysis.....	15
4.1. Total oxidisable precursors assay (TOPA).....	15
4.2. Total organic fluorine (TOF) and total fluorine (TF).....	16
5. Conclusion.....	18
Declaration of competing interest.....	19
Acknowledgements.....	19
References.....	19

1. Introduction

1.1. PFAS

'Per-and polyfluorinated alkyl substances', is used as a generic term for highly fluorinated aliphatic substances consisting of at least one fully-fluorinated carbon atom ($-CF_2-$) (Ullah et al., 2011). In addition to the fully or partially fluorinated alkyl chain, the substance usually contain a terminal functional group such as a carboxylate, sulphonamide, phosphonate, sulfonate or alcohol (Buck et al., 2011; Ding et al., 2013). Unfortunately, the high C-F bonding strength (485 kJ/mol) makes PFAS thermodynamically stable and highly resistant in hydrolysis, metabolism, photolysis, and other forms of degradation (Boiteux et al., 2012). Additionally, because of their high stability, and water/lipid repellent properties, PFAS exhibit unique physical, chemical, and biological properties. Such properties attract wide use of PFAS for various purposes in our everyday lives, such as protective coatings and firefighting materials (Buck et al., 2011). Due to their widespread use, PFAS have entered our environment as emerging contaminants and their monitoring is thus vital to facilitate environmental management and remediation.

Owing to the persistency of PFAS, they might be accumulated even at a trace level in different environmental compartments, which make them difficult to analyse. Thus, most of the analysis are carried out using liquid chromatography-mass spectrometry (LC-MS) in professional laboratory. Whether it is possible or not to conduct on-site analysis, or at least for pre-screening, is an interesting topic. In the meantime, considering the diverse environmental matrices, the sample preparation plays the vital role towards the analysis success, which has been significantly advanced recently. However, there is no critical review in this field. Another analysis challenge is that, currently limited number of PFAS (~28) are being analysed quantitatively, while there are around 5000 of PFAS on the global market (FDA, 2019), most of which are "unknown" and generally called as "PFAS precursors". How to analyse those "unknown precursors" will also be discussed here. Recently, the analysis on the short-chain PFAS also has gained momentum and will be reviewed too.

Therefore, the review is designed accordingly, (Part 1) a brief summary of PFAS contamination; (Part 2) the current analysis methodologies, mainly chromatography, with reference to its selectivity and sensitivity, with focus on the sample preparation and the analysis of the new/short-chain PFAS study; (Part 3) the possibilities of nano sensors and smartphone device/or the mobile application or "app" for on-site pre-screening analysis; (Part 4) total oxidisable precursor assay (TOPA), total fluorine (TF) and total organic fluorine (TOF) for quantification of PFAS precursors and mass balance analysis are critically reviewed and presented here.

1.2. Classification of PFAS

Generally, PFAS can be classified into long chain ($C \geq 8$) and short chain ($C < 8$), based on number of fluorinated-carbon atoms present in their backbone, the fully or partially fluorinated alkyl chain. The former includes perfluoroalkyl carboxylic acids (PFCA, $C_nF_{2n+1}CO_2H$, ($n \geq 7$), such as perfluorooctanoate acid, PFOA) and perfluoroalkane sulfonic acids (PFSA, $C_nF_{2n+1}SO_3H$, ($n \geq 8$), such as perfluorooctane sulfonate, PFOS) (Buck et al., 2011). The latter includes GenX, PFCA ($n < 7$, such as Perfluorohexanoic acid, PFHxA) and PFSA ($n < 8$, such as perfluorobutane sulfonate, PFBS) (Brendel et al., 2018; OECD, 2015). In terms of the terminal functional groups, besides the carboxylic acids and sulfonic acids, other types include perfluoroalkane sulfonamido substances, perfluoroalkane sulfonamido ethanols /acrylates etc. (Buck et al., 2011; Nakayama et al., 2019). In addition, fluorotelomer-based backbone with terminal groups including betaines, sulfonamido betaines, thioamido sulfonates, sulfonamido amines, thiohydroxy ammonium, etc. are some of newly identified PFAS (Backe et al., 2013). The miscellany of PFAS and their yields are described in Table 1 and supporting information.

2. Chromatography techniques for PFAS analysis

Different types of chromatographic techniques have being employed for PFAS analysis, such as liquid chromatography (LC) including high performance liquid chromatography (HPLC), ultra-high-performance liquid chromatography/or ultra-performance liquid chromatography (UHPLC/UPLC), capillary liquid chromatography (CLC), and gas chromatography (GC). The traditional-HPLC is regularly used for the analysis of ionic PFAS (i.e. PFCA, PFSA), where GC is a convenient tool for volatile and semi-volatile PFAS analysis (i.e., fluorotelomer alcohols, FTOH; perfluorinated sulfonamido ethanols, FASE)

Table 1
Determination of PFAS in different matrices using LC /GC–MS techniques.

Techniques	Major features				
LC-MS	<ul style="list-style-type: none"> Analytes are identified based on different types of LC detector within the chromatographic ranges Analyser/detector: Single/triple quadrupole MS, time-of-flight (ToF), ion-trap, combine with ToF and MS 				
GC-EI-MS	<ul style="list-style-type: none"> Detect and quantify volatile, semi-volatile and neutral PFAS such as FTOH, FOSES and FOSAs etc. Analyser/detector: Double/quadrupole-MS, NCI/ PCI/ FID/ TCD 				
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
PFHxS, PFOS, PFDS, PFOA, fluorinated alkylpolyglycol ether PFHxA, PFHpA, PFTrDA, PFUnDA, PFOA, PFDoA, PFOA, PFDA, PFUnA, PFDoA, PFTA, PFDS, PFNA, PFOS, PFHxS, N-Et-FOSAA, N-Me-FOSAA	LC/(-)ESI-MS/MS, GC/ECD, flow injection-MS/MS LC/(-)ESI-MS/MS LC/(-)ESI-MS/MS	Hot vapour /Soxhelt extraction & PLE d-SLE SLE	6000–10,000 ng/g dw 1 ng/g (LOQ) 0.011–2.2 ng/g	Sediment Soil, sediment and sludge Sediment, sludge	Schröder (2003) Powley et al. (2005a) Higgins et al. (2005)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
PFOA, PFDA	GC-NCI/MS	PLE and SPME	0.5–0.8 ng/g	Harbour sediment	Alzaga et al. (2005)
PFHS, PFBS, PFOSA, PFOS, PFNA, PFDA, PFUnDA, PFDoDA, PFTDA, PFHxDA, PFOcDA, PFOA, 8:2 FTUCA, 8:2 FTCA, PFOA, PFNA, PFDA	LC/(-)ESI-MS/MS LC/(-)ESI-MS/MS	SPE SLE	10–25 ng/g 0.6 ng/g	STP sludge Soil	Sinclair and Kannan (2006) Washington et al. (2007)
PFXA, PFHA, PFOA, PFNA, PFDA, PFOA, PFHxA, PFDoA	LC/(-)ESI-MS/MS GC/EI-MS	SLE SPE	14 fg 36,000 ng/L (LOQ)	Soil Ground water	Washington et al. (2008) Moody and Field (1999)
PFOA, PFOS	LC/(-)ESI-MS/MS	SPE	10–50 ng/L (MQL)	River water	Hansen et al. (2002)
PFPeA, PFHxA, PFHpA, PFOA, PFDoA, PFBS, PFHxS, PFOS	LC/(-)ESI-MS/MS ¹⁹ F-NMR	SPE	9–17 ng/L (LOQ) 10,000 ng/L (MDL)	Surface water	Hansen et al. (2002) and Moody et al. (2001)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
PFBS, PFHxS, PFOS, PFOA, PFNA, PFOSA, PFOA, PFOS	LC/(-)ESI-MS/MS LC/(-)ESI-MS/MS	SPE SPE	0.0001–0.0052 ng/L (LOD) 10–50 ng/L (MQL)	Surface and deep seawater River water	Yamashita et al. (2004) Hansen et al. (2002)
PFBS, PFOS	LC/(-)ESI-MS/MS	–	25,000 ng/L (LOQ)	Ground, river and tap water	Hebert et al. (2002)
PFOS	LC/(-)APPI-MS	Turbulent flow chromatography based online extraction	5.35 ng/L (LOD)	River water	Takino et al. (2003)
PFOA, PFOS, PFOSAA, N-Et-FOSAA, FOSA, N-Et-FOSA, N-Et-FOSE, PFOS, PFOA, PFNA, PFDA, PFUnA, PFDoA, 6:2, 8:2, 10:2 FTCA, 6:2, 8:2, 10:2 FTUCA, PFBS, PFHxS, PFOS, 4:2, 6:2, 8:2 FTS	LC/(-)ESI-MS LC/(-)ESI-MS/MS LC/(-)ESI-MS/MS	SPE SPE –	0.2–13 ng/L (LOQ) 0.04–7.2 ng/L 470–5000 ng/L (LOQ)	Surface water Rain water Ground water	Boulanger et al. (2004) Loewen et al. (2005) Schultz et al. (2004)

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(Jahnke and Berger, 2009). Although capillary electrophoresis (CE) has also been applied for ionised and polar PFAS analysis, the sensitivity and the detection limit are not comparable with HPLC (Trojanowicz and Koc, 2013). Therefore, CE will not be discussed in this review.

Table 1 (continued).

Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
PFOS, PFOA, PFNA, PFDA, PFUnA, PFHxA, PFHpA	LC/(-)ESI-MS	SPE	0.28–0.58 ng/L (LOQ)	Surface water	Simcik and Dorweiler (2005)
PFOS, PFDS, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDaA	LC/(-)ESI-MS/MS	Automated SPE, LLE	0.2–6.4 ng/L 0.26–4.4 ng/L (MDL)	STP effluent	González-Barreiro et al. (2006)
PFOA, PFOS	Nano-LC/nano(-)ESI-MS	Online-SPE	0.5–1 ng/L	River water	Wilson et al. (2007)
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA	GC/MS	LLE	0.5 ng/L	STP effluent, surface and rain water	Scott et al. (2006)
PFHeA, PFOA, PFNA, PFDeA, PFOS	LC/(-)ESI-MS/MS	SPE	0.05–0.28 ng/L (MDL)	River and wastewater	Zhao et al. (2007)
PFOS, PFHxS, PFBS, PFOSA, PFOcDA, PFHxDA, PFTeDA, PFDaDA, PFUnDA, PFDA, PFNA, PFOA, PFHpA, PFHxA, PFPeA, PFBA, N-Et-FOSA, N-Et-FOSAA, 8:2, 10:1 FTOH, 8:2 FTCA, 8:2 FTUCA	LC/(-)ESI-MS/MS	SPE	0.016–0.1 ng-F/L (LOQ)	Coastal water	Miyake et al. (2007a)
PFOS, PFOA	LC/(-)ESI-MS/MS	SPE	0.26–22 ng/L and 5.2–92 ng/L; 0.16–22 ng/L and 2.3–84 ng/L	Fresh water Tap water	Takagi et al. (2008)
PFBS, PFHxA, PFHpA, PFOA, PFNA, PFOS	LC/(-)ESI-MS/MS	Automated solid phase extraction	0.2–100 ng/L	River water	Loos et al. (2017)
PFBA, PFPeA, PFHxA, PFHpA, PFOA, 4:2 FTSA, 6:2 FTSA	LC/GC-MS/MS	SPME	13–131.9 ng/L	Surface, drinking and river water	Boiteux et al. (2017)
PFOS, PFOA, PFHxA, PFHpA, PFHxS, PFPeA, PFBA, PFNA, PFDA, PFBS	LC/(-)ESI-MS/MS	Automated SPE	Max. 76 ng/L	Fresh and treated water	Boiteux et al. (2012)
4:2, 6:2, 8:2 FTAAoS, 4:2, 6:2, 8:2 FtS, PFBSaAm, PFPeSaAm, PFHxSaAm, PFBS, PFOSaAm, PFBSaAmA, PFOS, PFPeSaAmA, PFHxSaAmA, PFBA, PFHpS, PFDS, PFHxS, PFOSaAmA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDaA, PFTrA, PFTeA	LC/(-+)ESI-MS/MS	Micro-LLE	0.71–67 ng/L (MDL)	Ground water	Backe et al. (2013)
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDaDA, PFTrDA, PFTeDA, PFBS, PFHxS, PFOS, PFDS, FOSA, 6:2FTSA, 6:2FTUA, 8:2FTUA, 5:3FTCA, PFOAB	UHPLC-HRMS	Automated off line SPE	Up to 39 ng/L	Drinking water	Kaboré et al. (2018)

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Both of these techniques (i.e.; LC and CE) require highly sophisticated instruments and their analysis is generally time-consuming (Fang et al., 2017). A colouration, on the other hand, is applied to monitor PFAS through the methylene blue active substance (MBAS) assay (Fang et al., 2015; George and White, 1999). The method is performed upon the interaction between anionic surfactant and cationic dye, subsequently analysed using UV-Vis spectrometer or on-site testing kit (Fang et al., 2016a). Those techniques usually detect high concentration of PFAS (> 10 ppb, parts per billion) and will be discussed in the following section (Part 3).

Table 1 (continued).

PFHxS, PFHpA, PFOA, PFOS, PFNA, PFDA	LC/(-)ESI-MS/MS	Bamboo-charcoal based SPE	0.01–1.15 ng/L	Drinking, tap, lake and pond water	Deng et al. (2018)
PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFTTrDA, PFTeDA, PFHxDA, PFODA	LC/(-)ESI-MS/MS	Solid phase extraction	0.48–1.68 pg/inject	Estuarine water	Mulabagal et al. (2018)
PFOA, TFA, PFPrA, PFBA, PFPeA, PFHxA, PFHpA	LC/(-)ESI-MS/MS	SPE	0.1–3.3 ng/L	Surface, ground and drinking water	Janda et al. (2019a)
PFOSA, N-Et-PFOA	GC/P IC-MS	SLE	0.1–0.25 ng/L (MDL)	Fast food and fish	Tittlemier et al. (2005)
PFOS, PFHS, PFBS, PFUnDA, PFDA, PFNA, PFOA, PFHpA, PFHxA	LC/(-)ESI-MS/MS	IPE	0.25 ng/L (LOQ)	Seafood	Gulkowska et al. (2006)
PFOS, PFHpA, PFDoDA, PFTeDA	LC/(-)ESI-MS/MS	SLE	0.5–6 ng/g	Meat, fish, fast food and food packaging materials	Tittlemier et al. (2007)
PFOS, PFOA, PFDA, PFPA, PFBS, PFNA	LC-QqLIT-MS	PLE & SPE	0.003–0.05 µg/kg (LOQ)	Fish	Llorca et al. (2009)
PFOA, PFOS	LC/(-)ESI-MS/MS	LLE	7.5 µg/kg	Fish	Nania et al. (2009)
PFOA, PFOS, PFNA, ip-PFNA, PFDA, PFDS	LC-QqLIT-MS	SPE	1.2–362 ng/g (MLOD)	Baby foods	Llorca et al. (2010)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
PFBS, PFOA, PFDA, PFUnA, PFTeA, PFHxA, PFHxS, PFOS	LC/(-)ESI-MS/MS	Micro-extraction	0.4–6 ng/g	Muscle and liver of fish and bird	Luque et al. (2010)
PFOA, PFOS	LC/(-)ESI-MS/MS	SPE	5.4–17.2 ng/g	Commercial fish	Squadrone et al. (2015)
PFBA, PFHxPA, PFPeA, PFBS, PFHxA, PFOPA, PFHpA, PFHxS, PFOA, PFDPA, PFNA, PFOS, PFOSA, PFDA	LC/(-)ESI-MS/MS	Focused ultrasound solid–liquid extraction (FUSLE) and SPE	0.3–12.4 ng/g (MDL) 0.2–12.5 ng/g (MDL)	Vegetables Fish Soil	Zabaleta et al. (2014)
PFOS, PFOA, PFHxS, PFHxA, PFOSA	LC/(-)ESI-MS/MS	SLE	0.05–0.2 ng/L	Food ingredients	Fromme et al. (2007)
PFBA, PFPeA, PFHxA, PFHpA, PFNA, PFDA, PFBS, PFHxS, PFOS, PFOSA, PFHxPA, PFOPA, PFDPA	LC/(-)ESI-MS/MS	Focused ultrasonic solid–liquid extraction (FUSLE)	1.4–8 ng/g	Muscle and liver of fish	Zabaleta et al. (2015)
PFOA	LC/(-)ESI-MS/MS	SLE	1–3 ng/g (LOQ)	Textile and carpet	Mawn et al. (2005)
PFOA	LC/(-)ESI-MS/MS	SPE, PLE	10–100 pg/m ²	Cookware	Powley et al. (2005b)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
PFOA, PFOS, N-Et-FOSA, N-Et-FOSE, N-Et-FOSAA, PFOSAA, PFOSA, PFOSE 4:2, 6:2, 8:2, 10:2, 12:2 FTOH, N-Me-FOSE	LC/(-)ESI-MS/MS	–	–	Scotch Gard	Boulanger et al. (2005)
	LC/EI-MS, GC/PCI-MS	XAD extracted with EtOAc	2.5–25 ng/µL (LOQ)	Polymeric and surfactant material	Dinglasan-Panlilio and Mabury (2006)

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For the sensitive and selective detection of PFAS using LC (usually coupled with mass spectrometry (MS) detector, LC-MS), EPA 537, EPA 537.1 and ASTM D7979-17, ASTM D7968-17a have been developed by the United States Environmental Protection Agency (US EPA) and the American Society for Testing and Materials (ASTM), respectively. In addition to the analysis of PFAS, before conducting any instrumental test, sample preparation and/or pre-treatment process is typically required. For instance, to enhance selectivity, sensitivity and clean-up of target analysts from the sample background, several form of extraction techniques such as solid phase extraction (SPE), liquid–liquid extraction (LLE), solid phase micro

Table 1 (continued).

N-EtPFOSA, PFOSA, N, N-Et-PFOSA, N-Me-PFOSA, N, N-Me-PFOSA	GC/PIC-MS	SLE	0.1–0.25 ng/L (MDL)	Food packaging materials	Tittlemier et al. (2006)
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFBS, PFHxS, PFOS, PFTrDA, PFTeDA, PFHxDA, PFODA, PFDS	LC/(-)ESI-MS/MS	PLE	5–30 ng/g	Food packaging materials	Zafeiraki et al. (2014)
PFBS, PFHxS, PFOS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxPA, PFOPA, PFDPA, PFOSA, 6:2 FTCA, 8:2 FTCA, 5:3 FTCA, 7:3 FTCA, 6:2 FTUCA, 8:2 FTUCA, 6:2 mono & di PAP, 8:2 mono & di PAP	LC-QqQ-MS/MS	Ultrasonic probe-assisted extraction (UPAE)	0.6–2.2 ng/L	Plastic and cardboard materials	Zabaleta et al. (2016)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
6:2, 8:2 FTOH, PFOA	LC/(-)ESI-MS/MS GC-MS	SPE, SLE, XAD with MeOH	2.5–25 ng (LOQ)	Popcorn bag, cookware	Sinclair et al. (2007)
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFTrDA, PFTeDA, PFHxDA, PFODA, 8:2 FTCA, 4:2/6:2/8:2 FTS	LC/GC-MS/MS	SPE	–	Household products	Favreau et al. (2017)
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFTrDA, PFTeDA, PFHxDA, 8:2 FTCA, 10:2 FTCA, 8:2 FTUCA, 10:2 FTUCA, 7:3 FTCA, 9:3 FTCA, 5:3 FTUCA, 7:3 FTUCA, 9:3 FTUCA	LC-QToF-MS	Focused ultrasonic solid-liquid extraction (FUSLE)	0.6–2.2 ng/g (MDL)	Popcorn bag	Zabaleta et al. (2017)
PFOA	LC/(-)ESI-MS/MS	SLE	1–2 ng/g	Paper, textile	Stadalius et al. (2006)
PFOA, PFHA, PFOS	LC/(-)ESI-IT-MS/MS	Online extraction	0.2–0.5 ng/mL	Human plasma	Holm et al. (2004)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
PFOS, PFNA, PFOA	LC/(-)ESI-MS/MS	SPE	0.1–0.2 ng/mL (LOQ)	Human liver, brain and kidney	Maestri et al. (2006)
PFOS, PFOA, PFOSA	LC/(-)ESI-MS LC/(-)ESI-MS/MS	Online SPE Automated SPE	0.5–1 ng/mL (LOQ) 0.1–3.2 ng/mL 0.1–1 ng/mL	Human plasma Human serum Breast milk	Inoue et al. (2004) Kuklenyik et al. (2004)
Me-PFOSA-AcOH, Et-PFOSA-AcOH, PFHxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDeA, PFUA, PFDoA	LC/(-)ESI-MS/MS	–	0.5 ng/mL (LOQ)	Human blood	Flaherty et al. (2005)
PFOA, PFOS, PFAD	LC/(-)ESI-MS/MS	MTBE	0.02–0.18 ng/mL	Human serum	Wu et al. (2017)
PFBS, PFHS, PFOS, PFOA	LC/(-)ESI-MS/MS	SPE	1 ng/mL (LOQ)	Human serum, blood and plasma	Ehresman et al. (2007)
PFOS, PFHS, PFOA	LC/(-)ESI-MS/MS	–	0.5–1.6 ng/mL (LOQ)	Human serum	Olsen et al. (2007a)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
PFHxS, PFOS, PFOA, PFNA, PFDA, PFUnDA, PFDoDA	LC/(-)ESI-MS/MS	–	52–1.9 ng/L	Human blood	Lindh et al. (2012)

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Table 1 (continued).

PFOA	LC/(-)ESI-MS/MS	-	1.0 ng/mL	Human plasma	Olsen et al. (2007b)
PFOS			3.4 ng/mL		
PFOA	LC/(-)ESI-MS/MS	LLE	0.5 ng/mL	Human serum	Rogatsky et al. (2017)
6:2 PAP, 8:2 PAP, 6:2 diPAP, 8:2 diPAP, PFHxPA, PFOPA, PFDPAA, PFBS, PFHxS, PFHpS, PFOS, PFDS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTTrDA, PFTeDA, PFOSA, MeFOSA, EtFOSA PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTTrDA, PFTeDA, PFHxDA, PFOcDA, PFBS, PFHS, PFOS, PFDS	LC/(-)ESI-MS/MS	Online solid phase extraction	0.0018–0.09 ng/mL	Human serum, plasma and whole blood	Poothong et al. (2017)
	LC/(-)ESI-MS/MS	MTBE	0.025–0.01 ng/mL (LOQ)	Breast milk	Lee et al. (2018)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
N-Et-FOSA, N-Me-FOSE, N-Et-FOSE, 4:2, 8:2, 10:2 N-Et-FOSE	GC/PCI-GS, GC/NCI-GS	-	0.15–6.2 pg/m ³	Outdoor air	Martin et al. (2002)
PFOA, PFOS	LC/(-)ESI-MS/MS	SLE	10–50 ng/g (LOQ)	Dust	Moriwaki et al. (2003)
N-Et-FOSA, N-Et-FOSE, N-Me-FOSEA	GC/EI-MS, GC/NCI-GS	Soxhlet extraction	<0.3–20 pg/m ³ (MDL)	Indoor and outdoor air	Shoeib et al. (2004)
N-Et-FOSA, N-Me-FOSE, N-Et-FOSE, N-Me-FOSEA	GC/EI-MS, GC/NCI-GS	Soxhlet extraction	0.01–7.1 pg/m ³ (MDL)	Indoor and outdoor air	Shoeib et al. (2005)
PFOA, PFOSA, PFOS, PFBS, PFHS	LC/(-)ESI-MS/MS	SLE	1.2–6.1 pg (LOD) 0.99–4.56 ng/g (MDL)	Dust Dust	Kubwabo et al. (2005)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
PFOS, PFOA, N-Et-FOSA, N-Me-FOSE, N-Me-FOSAA, PFOSAA, PFOSA	LC/(-)ESI-MS	Solvent extraction	-	Outdoor air	Boulanger et al. (2005)
N-Me-FOSEA, N-Me-FOSE, N-Et-FOSE, 6:2, 8:2, 10:2 FTOH	GC/EI-MS, GC/PCI-MS	Soxhlet extraction	0.001–3.5 pg/m ³ (MDL)	Outdoor air	Shoeib et al. (2006)
N-Me-FOSE, N-Et-FOSE, N-Me-FOSA, N-Et-FOSA, 4:2, 6:2, 8:2, 10:2 FTOH	GC/PCI-MS, GC/NCI-MS	Solvent extraction	0.2–2.5 pg/m ³ (MQL)	Outdoor air	Jahnke et al. (2007)
N-Me-FBSA, N-Me-FBSE, N-Me-FOSE, N-Et-FOSE, N-Me-FOSA, N-Et-FOSA, 4:2, 6:2, 8:2, 10:2, 12:2 FTOH	GC/PCI-MS, GC/NCI-MS	Solvent extraction	0.01–120 pg/m ³	Indoor and outdoor air	Barber et al. (2007)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
N-Me-FOSEA, N-Me-FOSE, N-Et-FOSE, 6:2, 8:2, 10:2 FTOH	GC/PCI-MS	Soxhlet extraction	-	Indoor air	Shoeib et al. (2008)

(continued on next page)

extraction (SPME), and dispersive liquid–liquid micro extraction (DLLME) are commonly involved. The analysis procedure is schematically presented in Fig. 1.

2.1. Liquid chromatography (LC)

HPLC with a UV (ultraviolet) detector was previously used to detect both long ($C \geq 8$) and short chain ($C < 8$) PFAS (i.e., PFHxA, PFHpA, PFOA, PFNA and PFDA) in the liver samples of rat using a fluorescence based

Table 1 (continued).

PFBS, PFPS, PFHxS, PFHpS, PFOS, PFNS, PFDCs, PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, 4:2, 6:2, 8:2, 10:2 FTOH, N-Me-FOSE, N-Et-FOSE, N-Me-FOSA, N-Et-FOSA, 6:2, 8:2 FTS 8:2 FTO, 6:2, 8:2 FTA, 4:2, 6:2, 8:2, 10:2, 12:2 FTOH, N-Me-FBSA, N-Me-FOSA, N-Et-FOSA, N-Me-FBSE, N-Me-FOSE, N-Et-FOSE	LC-QTOF-MS, GC/PCI-MS, GC/NCI-MS	Solvent extraction	0.5–81.1 ng/L 25 ng/L	House dust Air	Huber et al. (2011)
n:2 FTOHs (n = 6, 8, 10), MeFOSA, EtFOSA, MeFOSE, EtFOSE	GC/PCI-MS	Cold column extraction	0.09–1.85 pg/m ³ (MDL)	Air	Li et al. (2011)
PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFOS, PFHxS, PFBS, MeFOSA, EtFOSA, EtFOSE, MeFOSE, n:2 FTOHs (n = 6, 8, 10), n:2 FTUCAs, n:2 diPAPs (n = 6, 8)	GC/PCI-MS HPLC/(-) ESI-MS/MS	SPE	0.9–26.3 pg/m ³ (MDL)	Indoor air	Yao et al. (2018)
Identified PFAS*	Analysis approaches	Extraction methods	Detection limit (LOD/LOQ/MDL/MQL)	Sources	References
6:2, 8:2, 10:2 FTOH, Me-FOSA, Et-FOSA, 6:2 FTMAC, 8:2, 10:2 FTAC, 6:6, 6:8, 8:8 PFPIA, 6:2, 8:2 monoPAPs, 6:2, 8:2 diPAPs, PFOS, PFOA, PFDS, PFBS, PFHxS	LC/(-)ESI-MS/MS, GC/PCI-MS	Soxhlet extraction, SPE	0.29–2.40 ng/g	Indoor dust and packaging materials	Shoeib et al. (2016)

3-bromo-acetyl-7-methoxycoumarin (BrAMC) substance (Ohya et al., 1998). Soon after, LC-MS/MS (mass spectrometry/mass spectrometry) was introduced to detect trace levels of PFOA, PFOS and PFHxS by Hansen et al. (2001). After homogenisation, samples were extracted through liquid phase extraction (LPE), with PFAS detected in the ranges of 2 ng/g – 8.5 ng/g (ppb) in liver and 1 ng/g – 2 ng/g (ppb) in blood serum.

Considerable advances have been made since then, including (i), in order to get more exactitude and maintain an optimal analytical outcomes, different types of isotope internal standards (IS) have been used for the quantitative analysis. For example, ¹³C₂-PFOA was applied as an IS for PFAS screening in different human and animal tissues (Kuklenyik et al., 2004; Taniyasu et al., 2005; Verreault et al., 2005). (ii), different sample preparation procedures have been introduced for selective and sensitive analysis of target compounds from different matrices, which are reviewed and described in the following sections. Application of LC-MS to identify and quantify of PFAS from 1985 to 2019 are well summarised in Table 1; with their detectors, sources, limit of detection (LOD) and extraction methods.

2.1.1. Analysis of PFAS in solid matrices

In general, when solid samples are collected, they need to be dried, sieved (usually for soil, sand and sediment), homogenised, extracted, and concentrated prior to the HPLC-MS analysis. In order to eliminate background interference and increase higher recovery different types of pre-treatment methods need to be applied.

Higgins et al. (2005) implemented LC-MS/MS to detect 12 PFAS in sediment and domestic sludge, in the ranges of 0.04–0.246 ng/g (ppb) and 0.7–2.2 ng/g (ppb), respectively. Analytes were extracted by solid-liquid extraction (SLE) in ultra-sonication with methanol: water (9:1) and 0.1% acetic acid. Extracts were then purified by SPE using C18 sorbent.

Bao et al. (2010) implemented HPLC-MS/MS with negative electrospray ionisation (-ESI) for the analysis of 8 PFAS in river sediments. The sample was extracted by tetrabutylammonium hydrogensulfate (TBAHS) and sodium carbonate (Na₂CO₃) (1:5). Concentration was estimated from 0.09 ng/g to 3.6 ng/g (ppb) and the recoveries reached up to 108%. In regard to the extraction of PFAS in sediments (Chen et al., 2011), SLE was employed followed by SPE clean-up protocol. Therefore, PFOA and PFOS was detected at 0.1–0.5 ppb and 0.1–2.0 ppb, respectively.

Li et al. (2017) performed UPLC/ESI-MS/MS to screen PFAS in sediment collected from different lakes. PFAS were extracted from dry sediment by ultra-sonication in methanol and obtaining the total concentration of PFAS from 0.61 ng/g to 26 ng/g (ppb). Additionally, excellent spike recoveries (88%–102%) without matrix effects proved method's validity and acceptability.

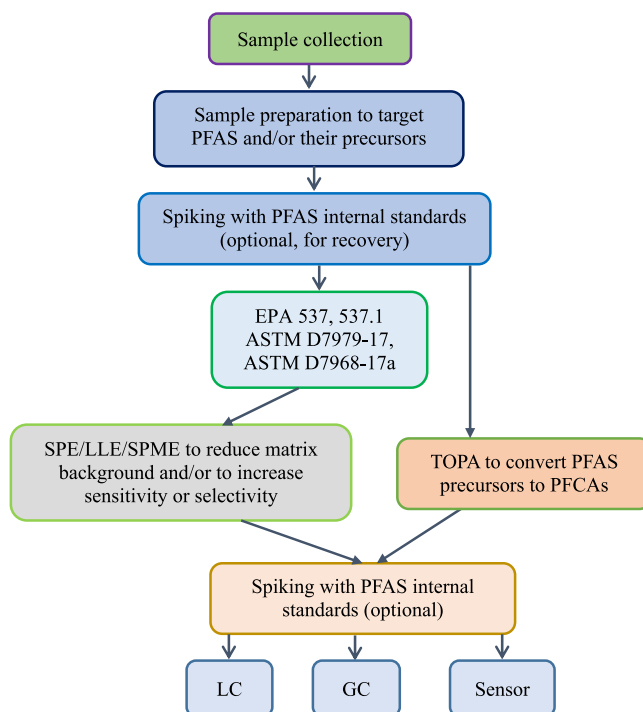


Fig. 1. Schematic of the general procedure for PFAS analysis.

Regarding multiple PFAS detection, Naile et al. (2010) described a method for the identification of 12 PFAS in different sources of soil and sediments. After homogenisation, samples were decanted in acetic acid and sonicated, followed by HPLC-MS/MS analysis. However, some compounds were demonstrated with low recoveries (20%, or even less), due to the hydrophobicity of solvents.

Wang et al. (2015) described a method for PFOS and PFOA identification in sewage sediment. Both of the compounds were extracted from high volume of sampling with methanol: acetic acid (9%:1%), using an SPE clean-up method. The PFAS was measured between 0.62 ng/g and 2.65 ng/g (ppb) by an HPLC-MS/MS. Yu et al. (2009) detected PFOA and PFOS in sludge. Target compounds were collected from two different municipal sewage treatment plants (STP). Prior to analysis by HPLC-MS/MS, samples were extracted and cleaned up by SLE and silica clean-up method, respectively. By doing so, they enhanced recovery performance (70%–84%) and reduced matrix interference.

Apart from this, AFFF (aqueous film-forming foam) amended soil has been paid attention and different types of PFAS have been detected. For example, target compounds were extracted with sequential extraction method (i.e. methanol vs. HCl-methanol vs. $\text{CH}_3\text{COONH}_4$ -methanol vs. NaOH). PFAS detection was done by ultra-high-performance liquid chromatography coupled to high resolution accurate mass, Orbitrap mass spectrometry (UHPLC-HRMS) (Munoz et al., 2018). Though the satisfactory recoveries (>90%) were shown for cationic and zwitterionic PFAS, lower recoveries (~12%) were observed for anionic PFAS.

2.1.2. Analysis of PFAS in aqueous matrices

Compared to solid samples where the level of PFAS is generally high (ppb or higher), the aqueous samples usually contain a low level of PFAS (sub ppb, or ppt, parts per trillion). Therefore, the sample preparation will pay more attention on the pre-concentration of PFAS and the clean-up of the sample background.

The presence of PFAS in the diverse forms of aqueous matrices including surface water, groundwater, drinking water, lake and coastal or sea waters, are not negligible. Newly identified PFAS compounds were detected in ground water using large volume injection-high performance liquid chromatography (LVI-HPLC) system (Backe et al., 2013), with help of micro liquid-liquid extraction (μ -LLE) method. The PFAS was detected in a range of 0.71 ng/L (ppt) to 67 ng/L (ppt). When pre-treatment methods such as filtration and centrifugation were involved, 40 new classes of PFAS were detected by high-resolution mass spectrometry with quadrupole time-of-flight mass spectrometry (QTOF-MS) in AFFF impacted groundwater (Barzen-Hanson et al., 2017).

A large number of PFAS precursors with different chain lengths and functional groups (i.e., anionic, cationic, zwitterionic, short and ultra-short chain) have been identified in drinking water (tap and bottle water) (Kaboré et al., 2018). Good recovery (~110%) and low matrix effect were observed. Additionally, ultra-short-chain PFAS (i.e., C_2 – C_3) were also detected by LC-QTOF-MS (Barzen-Hanson and Field, 2015) and ultra-performance convergence chromatography

(UPC²) coupled to a tandem mass spectrometer (Yeung et al., 2017) in AFFF impacted groundwater, river and rain water, respectively.

Shao et al. (2016) detected 11 PFCAs and 4 PFSA in surface and ground water, from an estuary precinct. Extraction was conducted with SPE (OASIS WAX) in methanol: H₂O. The PFAS was measured at 66.2 ng/L to 185 ng/L (ppt) (surface water) and 44.8 ng/L to 209 ng/L (ppt) (ground water), while analysis was run by HPLC-MS/MS. Gellrich et al. (2013) analysed 19 PFAS in tap and drinking water using UPLC-MS/MS. An excellent recovery (81% to 130%) was observed, while the analyst were extracted by SPE-Strata X-AW cartridges under the ultra-sonication treatment with methanol and deionised water (1:1). Similarly, short chain PFCAs (C₂-C₈) was identified in ground, surface and tap waters (Janda et al., 2019a). The extraction was involved with SPE using OASIS WAX and Strata X-AW, thus a recovery of 83%–107% was ensued at different pH (3–5) level.

Castiglioni et al. (2015) employed dual filtrating (cellulose membrane and glass microfibre filter GF/A) as the pre-treatment methods, before SPE with OASIS HLB cartridges. A rapid and straightforward technique was used to quantify short, long, legacy and emerging PFAS in estuarine surface water from different locations (Mulabagal et al., 2018). SPE (OASIS PRiME HLB) was employed to extract PFCAs, PFSA and perfluoro ethers, and they achieved a LOD in the range between 0.48 ng/L and 1.68 ng/L (ppt) with UHPLC/(-) ESI-MS/MS. The method was involved with small amount of sample, better recovery (78.54% to 112.61%), higher sensitivity and without significant matrix effects.

Recently, DLLME was also reported to extract different types of PFAS from tap, river water and urine samples (Wang et al., 2018b). In this method, extraction was conducted upon the fluoruous-fluoruous interactions, where perfluoro-tert-butanol was used as an extraction solvent and acetonitrile for solvent dispersion due to the immiscibility and miscibility behaviours. The method is very simple, cost effective, less time consuming and achieves sufficient recoveries (80.6% to 121%) for medium and long chain of PFAS. However, it is not suitable for the short chain PFAS as a low recovery (17% to 57%) is found. Similarly, a large number of PFAS (PFCAs (i.e., C₄-C₉, C₁₁-C₁₄, C₁₆), PFSA (i.e., C₄, C₇, C₈, C₁₀) and FOSA) were detected in snow, surface overflow, lake and costal sea water (Cai et al., 2012).

Liu et al. (2015b) described HPLC coupled to ultrahigh resolution orbit rap mass spectrometry (HPLC-uHRMS) for PFAS (C₅-C₁₇) monitoring. Samples were extracted from waste water via an on-line SPE using C18 sorbent. The method detection limits (MDLs) were estimated between 0.005 ng/mL to 0.2 ng/mL (ppb). The method is not only highly sensitive, but also rapid and more consistent, comparing to off-line pre-treatment methods. LC-MS/MS was applied to detect legacy and emerging PFAS in drinking, surface and waste water (Coggan et al., 2019) as well. Generally, SPE was used to extract the target analytes so that a good recovery (~134%) was obtained.

2.1.3. Analysis of PFAS in food matrices

Regarding food matrices, the sample preparation must focus on the extraction of PFAS, akin to solid samples. However, food matrices cover a range of complex targets, including fish, milk, seafood, vegetables oil, human breast milk and baby food etc.

LC-MS/MS was employed again to confirm the presence of PFSA and PFCAs in different food web by Tittlemier et al. (2007). After homogenisation and centrifugation target compounds were extracted by SLE with methanol and the LOD was reached from 0.5 ng/g to 6 ng/g. An UHPLC-MS/MS was employed with ¹³C₄-PFOS and ¹³C₄-PFOA as ISs to analyse a wide range of PFAS in raw and cooked fish samples (Gosetti et al., 2010). PFAS in raw samples were detected, but ultra-trace level detection was quite challenging from the cooked samples, thus PFAS appears to be released upon cooking the materials.

Additionally, ionic and non-ionic (i.e., PFCAs, PFSA, PFPAs, and FOSA) PFAS were detected in fish and milk samples (Lacina et al., 2011). Dispersive-SPE was used followed by C18 sorbents, ENVI-carb along with 'QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe)' clean-up method to reduce matrix effect and remove the co-extracts. Therefore, higher recoveries (70%–120%) were achieved. Another method was introduced to identify the presence of PFAS in diverse food items, which were collected from several countries (Hlouskova et al., 2013). Samples were homogenised, filtered, and subsequently extracted with QuEChERS method. In the meantime, C18 silica and ENVI-carb sorbent were applied as an additional clean-up step, ensuing the sufficient recoveries (73% to 128%).

Furthermore, PFAS was analysed in different Norwegian seafood by Berger and Haukås (2005). Ion-pair extraction (IPE) was used and followed by methanol: water with ammonium acetate in ultra-sonication and the target compounds were detected by HPLC/time-of-flight (TOF)/mass spectrometry (MS) (HPLC-TOF-MS) techniques. In addition, to increase the recovery, IPE is recommended for the short chain PFAS, while some optimisation are required to long chain PFAS.

Analysis of PFOA and PFOS in vegetable oils was carried out by Tang et al. (2014). They used reverse phase liquid-liquid extraction (RP-LLE) with methanol:H₂O and dichloromethane as a pre-treatment process and concluded that it enhanced extraction the efficiency and accuracy of target analytes. A method was described by Capriotti et al. (2013) to detect 12 PFAS in cow milk. Before running SPE with acetone to extract and clean-up using a graphitised carbon black column, samples were properly digested under an acidic and alkaline environment. Accordingly, a better recovery (91%–105%) of extracts without matrix effect were achieved.

Similarly, another method was reported for the determination and quantification of PFAS in human breast milk and baby food (Lankova et al., 2013). Dispersive solid phase extraction (D-SPE) was included as an extraction method, whereas C18 sorbent was introduced to purify and clean-up some crude extracts (i.e., fat and lipophilic compounds). The method offers a good sensitivity (3–200 pg/mL (ppt) in milk and 5–450 pg/g (ppt) in infant food materials), excellent recoveries (up to 117%), and less time (10 samples/hour).

2.1.4. Analysis of PFAS in biological matrices

Bio-samples from humans are highly complex matrices. Therefore, special care should be taken in the digestion and the extraction of PFAS from serum, liver, sera, hair, and other tissue.

Humans can be exposed to PFAS through the inhalation of polluted dirt (Cunha et al., 2010; D'Hollander et al., 2010; Tian et al., 2016), ingestion of contaminated food (Ericson et al., 2008; Van Leeuwen et al., 2009; Yuan et al., 2016), and/or drinking polluted water (Banzhaf et al., 2017; Wilhelm et al., 2015). An early analytical method was reported by (Olsen et al., 2003) to detect PFAS in human serum and liver. PFAS were extracted using an IPE method and the LOQ reached 6.1 ng/mL to 58.3 ng/mL (ppb) and 4.5 ng/g to 57 ng/g (ppb) in serum and liver samples, respectively. A method along with an automated SPE was described for monitoring PFCAs (C₈), PFSAs (C₂) and perfluorosulfonamides (C₃) in milk and human serum as well.

The IPE combined with tetra butyl ammonium hydrogen sulphate and MTBE was used to extract PFAS in plasma, serum and human blood by Kannan et al. (2004). PFAS was estimated from 0.5 ng/mL to 100 ng/mL (ppb) using HPLC-MS and HPLC-MS/MS system. PFAS was also identified in the blood sample of human by Kärman et al. (2005). Here, heparin was added to the blood cell and SPE was conducted followed by ultra-sonication with formic acid.

An on-line SPE-HPLC-MS/MS was used to analyse PFAS in human sera (Yu et al., 2017). Target analytes were extracted from small volume of samples with a pair of SPE (HySphere PICO C18-SE and XDB (extra densely bonded) C18) cartridges, which allowed to acquire a better recovery. Likewise, an on-line SPE consisting of a Turboflow column was run by Gao et al. (2018) to extract a large number of PFAS and their derivatives from human sera at various pH levels.

PFAS was detected in pieces and powders of human hair by Kim et al. (2017). They used SPE, IPE, IPE and SPE, and liquid-liquid extraction (LLE) with an ENVI-carb clean-up procedure. All extraction was optimised successfully and completed using methanol: acetonitrile; tetra butyl ammonium hydrogen sulphate (TBAHS); MTBE and ethyl acetate. Among all the extractions (IPE, IPE + SPE, and solvent extraction with ENVI-carb clean-up), SPE was found to be more efficient to obtain higher recoveries (86%–102%).

A highly fluorour-affinity based DLLME technique was employed to extract targets from human urine by Wang et al. (2018b). The technique used less extraction solvent and significantly reduced the matrix effects because of its fluorophilicity. The limit of quantification (LOQ) was observed as 0.6 ng/L to 8.7 ng/L and higher recoveries were found (~122%) for the median and long chain of PFAS.

Additionally, to identify organic compounds in placenta, a method was published by Martín et al. (2016). Tissue was homogenised in acetonitrile under ultra-sonication, enriched using a C18 sorbent of a D-SPE system and further analysis was completed by a UHPLC-tandem phase MS system.

2.1.5. Analysis of PFAS in air, dust and other

Humans might be exposed to PFAS via indoor air, dust and other PFAS-containing products. For example, PFCAs were detected in carpet and carpet treatment products. Kim et al. (2015) investigated the leaching effect of PFAS in carpet at different temperature and pH. Target compounds were extracted by SPE (OASIS WAX) with methanol and formic acid, and the leaching concentration of PFCAs and PFSAs were quantified (6.75, 8.62 and 10.28 ng/L, ppt) using an HPLC-MS/MS system.

Different from other matrices, PFAS in air might be volatile or adsorbed onto the dust surface, which should be considered in extraction and sample preparation.

HPLC-MS/MS was used for determination of neutral and ionic PFAS in different environmental matrices of the textile industry (Heydebreck et al., 2016). Passive air, dust and airborne particles were collected via a polyurethane foam (PUF) disk. SPE (OASIS WAX) with ENVI-Carb and Soxhelt extraction used for these samples. Yao et al. (2017) analysed PFAS from a high sampling volume of air, which were enriched on XAD-2 resin/PUF and extracted with methanol. The extracts were cleaned up by a dispersive ENVI-carb clean-up protocol and the mass spectrometer and quantitative studies were done by a selective ion monitoring (SIM) and positive chemical ionisation (PCI) approach, respectively. To achieve maximum extracts in the target samples, solvent extraction was employed for PFSAs (C₄, C₆, C₇ and C₈) and PFCAs (C₄–C₁₄) analysis in outdoor clothing and jackets (van der Veen et al., 2016). Karásková et al. (2016) identified 20 PFAS in household dust using an HPLC/-ESI-MS/MS system. Samples were extracted using ammonium acetate and methanol in an ultra-sonication bath.

Generally, both active and passive air sampling are applied in indoor and outdoor air analysis. Though they have some limitations (i.e., large footprint, and time consumed in the pre-sampling and extraction techniques), but they are convenient and become popular for air sampling. Recently, Yao et al. (2018) designed a new SPE containing HC-C18 and WAX sorbents, which were used for neutral and ionisable PFAS analysis in indoor air and hotel dust. While it took considerable time for sample processing and incubating, the sorbents were efficient in extracting PFAS from the sources. Tian et al. (2018) determined 16 ionisable PFAS by HPLC-MS/MS in air samples. Passive sampling techniques was used to collect the air samples from landfill by using sorbent-impregnated polyurethane foam (SIP) disks, achieving a LOD of 9.5 ng/m³. A method was developed by Eriksson and Kärman (2015) to collect household dust from different countries. Subsequently, extraction and clean-up were conducted by SPE using OASIS-WAX and OASIS-HLB cartridges in ultra-sonication with methanol: water and ENVI-carb, respectively.

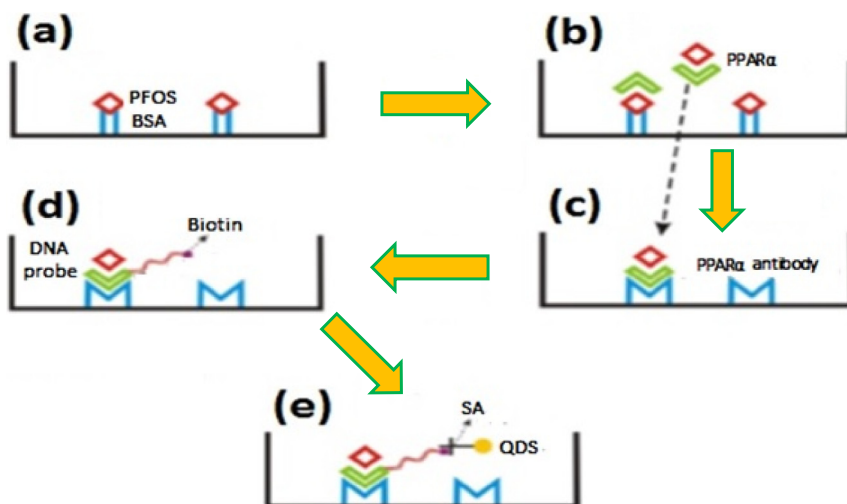


Fig. 2. Process of bioassay with QD-streptavidin-biotin-modified oligonucleotide probes. PFOS-BSA was placed on the surface of plate (a); PFOS standard or target sample and PPAR α -RXR α were added (b); Transferred supernatants onto the next plate, coated with PPAR α antibody (c); Added biotin modified probes (d); QDs-SA was added (e).

Source: The Figure was adapted with the permission from Zhang et al. (2011).

2.2. Gas chromatography (GC)

For the analysis of PFAS in air, gas chromatography-mass spectrometry (GC-MS) is applied to perform simultaneous separation and detection of volatile, semi-volatile and neutral PFAS (Nakayama et al., 2019; Trojanowicz and Koc, 2013), and PFAS from other matrices as well. The early analysis of PFAS using GC was reported by Ylinen et al. (1985) for urine and plasma samples. Studies of the identification and quantification of PFAS by gas chromatography (GC) (1985 to 2019) are also summarised (Table 1), including extraction, LODs, sources and detectors. Generally, GC analysis targets the volatile, semi-volatile and neutral PFAS, which limits its potential. Therefore, GC analysis of PFAS is not as popular as LC.

3. Sensors for PFAS detection

3.1. Nanoparticle-based sensor

Recently, nanoscale materials have emerged as an efficient and promising approach for the monitoring of contaminants. This is due to their excellent physical, chemical and optical properties; unique behaviours (aggregation, disaggregation, adsorption and desorption); small size (1 to 100 nm) and outstanding sensitivity. Therefore, different types of nano sensors, particularly nanoparticle (NP)-based sensors, have been developed for PFAS identification, as summarised in Table 2.

An early NP-based sensor was developed to trace PFAS in aquatic samples (Zhang et al., 2010). Nanoparticles were modified and functionalised with an octadecyl group. Subsequently, chitosan-coated magnetite nanoparticles (Fe₃O₄-C18-chitosan-MNPs) were used to extract PFOS, PFNA, PFDA, PFUnDA, PFDoDA and PFTA, from rain and tap water.

To analyse PFOS in river, lake and drinking bottle water, a quantum dot (QD) nanoparticle-based streptavidin labelling and bio-sensing system was developed by Zhang et al. (2011). Here, the target compound was bound to the hormone receptor of peroxisomal proliferator-activated receptor alpha (PPAR α), which formed a heterodimers with retinoid X receptors (RXR α) by the specific DNA sequence of peroxisome proliferator response elements (PPREs) inside the promotor region of certain genes. Later, it was induced to express gene at the transcriptional stage. The interaction between PFOS and PPAR α -RXR α occurred due to the size dependent luminescence properties of quantum dot nanoparticles (QDNPs) and streptavidin (SA) modified QDNPs that bind to the PPAR α -RXR α -DNA biomarker, labelled with biotin. The basic principle of the developed assay is shown in Fig. 2.

In another example, a QD-based sensor was described by Liu et al. (2015a), who used 3-mercaptopropionic acid (MPA) for the modification of cadmium sulphide (CdS)-QDs to determine PFOA in raw textile ingredients. In this method, MPA-CdS-QDs were dispersed and fluorescence intensity was quenched due to the adsorption of PFOA, which induced the aggregation of MPA-CdS-QDs by means of a fluoro-affinity interaction (Fig. 3).

Gold nanoparticles (AuNP) are widely used as nano sensors and they have been also prevalent in research on the PFAS sensing. Xia et al. (2011) developed a PPAR α responsive elements (PPRE) modified AuNPs sensor for the identification and quantification of PFAS in river water. The method is easy, convenient and highly sensitive as a LOD was obtained at

Table 2

Detection of PFAS using different types of nanoparticles, apps and others sensing methods.

Identified PFAS*	Nanoparticles with modified groups	Sensing types	Sensitivity	Sources	References
PFOS, PFNA, PFDA, PFTA PFUnDA, PFDoDA, PFOS	Magnetite nanoparticles (MNPs)	–	0.075–0.14 ng/L	Rain and tap water	Zhang et al. (2010)
	Quantum dots nanoparticles (QDNPs)	Optical	2.5 ppt	River, lake and bottle water	Zhang et al. (2011)
PFOA, PFOS	Gold nanoparticles (AuNPs)	Fluorometric	10 pM (~5 ppt)	River water	Xia et al. (2011)
PFOA	Thiol-terminated polystyrene modified gold nanoparticles (PS-SH-AuNPs)	Colorimetric	~100 ppm	–	Takayose et al. (2012)
Identified PFAS*	Nanoparticles with modified group	Sensing types	Sensitivity	Sources	References
PFOA, PFOS, PFHA	Molecularly imprinted polymer modified TiO ₂ nanotube arrays (MIP-TiO ₂ -NTAs)	Photoelectrochemical	85 ng/L	Tap, river and mountain water	Li et al. (2014)
PFOA	MPA-CdS-QDs	Fluorometric	0.3 μM (~120 ppb)	Textile ingredients	Liu et al. (2015a)
PFBS, PFHxS, PFHpA, PFOA, PFNA, PFTTrDA, PFTeDA, PFHxDA, PFOS, PFODA	Poly ethylene glycol and thiols modified old nanoparticles (Au-PEG-F-NPs)	Colorimetric	10 ppb	Tap and river water	Niu et al. (2014)
PFOA, PFPA, PFVA, PFHA, PFHpA, PFNA, PFDA, PFOS	MIP modified ultrathin nanosheet of carbon nitride (MIP-utg-C ₃ N ₄)	Electrochemiluminescence	0.01 ppb	Tap, river and lake water	Chen et al. (2015)
Identified PFAS*	Nanoparticles with modified group	Sensing types	Sensitivity	Sources	References
PFOA, PFOS, 1H, 1H, 2H, 2H perfluorooctanesulfonic acid (6:2 FTS)	MB/EV-FS-AgNPs-GO	SERS	50 ppb	Ground water	Fang et al. (2016a)
PFOA, PFOS, 1H, 1H, 2H, 2H perfluorooctanesulfonic acid (6:2FTS)	Molecular imprinted polymer (MIP)	Potentiometric	~41 ppb	Aqueous film-forming foams (AFFFs)	Fang et al. (2016a)
PFOS	Gold nanoparticles-polydopamine-polyvinylidene fluoride membrane chips along with surface-assisted laser desorption or ionisation-time-of-flight-mass spectrometry (AuNPs-PDA-PVDFM-SALDI-TOF-MS)	–	5.93–0.04 ng/mL	Tap, river and effluent water	Wang et al. (2018a)
Identified PFAS*	Nanoparticles with modified group	Sensing types	Sensitivity	Sources	References
PFOA, PFOS, PFAs	Molecularly imprinted polymer-surface plasmon resonance-plastic optical fibre (MIP-SPR-POF)	Optical	0.13–0.15 ppb	Water	Cennamo et al. (2018)
PFOA	Glass-chip-AIE	Fluorescence	41 ppb	Water	Fang et al. (2019)
PFOA	App based potable sensor	Colorimetric	10–0.5 ppb	Tap and ground water	Fang et al. (2018)

ppt (2.5 ng/L) level. Although the technique was based on an AuNP sensing platform, the use of Ag on the AuNP probe enhanced its sensitivity. However, an overnight incubation under 4 °C is a shortcoming of this assay.

Takayose et al. (2012) reported the use of thiol-terminated-polystyrene modified AuNP for visual detection of PFOA. In this approach, once the PFOA was added in an AuNP matrix solution, a thiol terminated polystyrene layer was replaced from the AuNP surface. Thus AuNPs were aggregated, due to the fluoro-phase attraction, and detection was achieved by observing the colour change from red to blue-purple. Similarly, Niu et al. (2014) developed polyethylene glycol (PEG-thiols) and perfluorinated thiols (F-thiols) modified AuNP. In his approach, a self-assembled monolayer

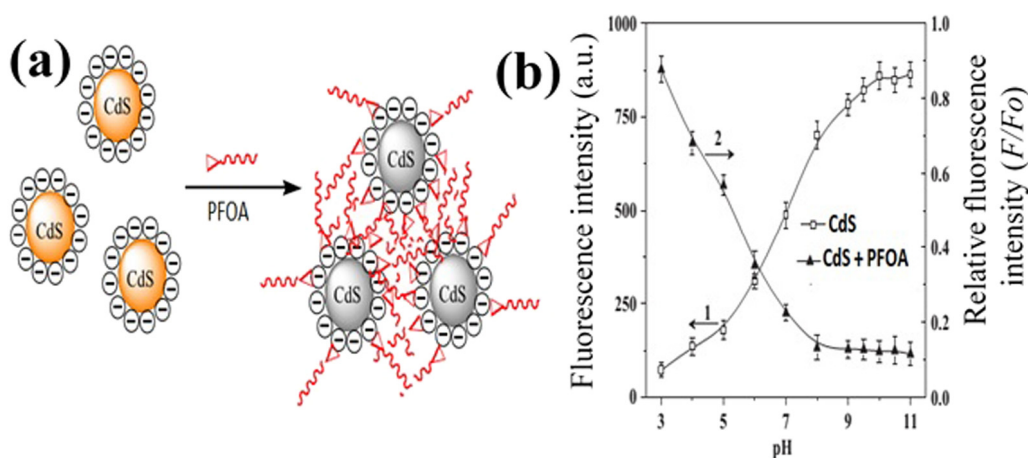


Fig. 3. Fluorometric detection of PFOA by quantum dot nanoparticles. (a) PFOA binds to the surface of MPA-CdS QDs. Before that, MPA-CdS QDs are well dispersed having strong fluorescence. After binding, PFOA induces aggregation of MPA-CdS QDs and thus fluorescence quenching. The effect on intensity of fluorescence at different pH is shown by the graph (b). However, 1 and 2 denotes the absence and presence of certain amount of PFOA, respectively.

Source: The Figure is adapted with the permission from Liu et al. (2015a).

(SAM) on the surface of AuNP provided the stability for its surface-functionalisation. After 0.5 h incubation with several fluoro-surfactants such as PFOS, PFOA and others, a LOD of 10 ppb was reached.

Wang et al. (2014) reported a very sophisticated and quick detection method by the aggregation of a multifunctional AuNP-polydopamine-polyvinylidene fluoro-membrane (AuNP-PDA-PVDFM). AuNP and polydopamine (PDA) were immobilised on the surface of the polyvinylidene fluoro-membrane (PVDFM) layer, thus analytes were extracted and enriched by the combination of PDA-PVDFM due to the π - π bond-stacking and hydrophobic interaction. Therefore, AuNP worked effectively as a matrix for the quick determination of PFOS in aquatic samples.

Encouraged by the high sensitivity of surface-enhanced Raman scattering (SERS), Fang et al. (2016b) developed a SERS-based method to detect fluorosurfactants (FS) in ground water samples. In this technique, silver nanoparticles (AgNPs) were used because of the high capacity for Raman enhancement. Methylene blue (MB) or ethyl violet (EV) was introduced into the aqueous solution, hence an immiscible ion-pair (with FS) was formed between the anionic surfactant and the cationic dye. In addition, graphene oxide (GO) was used to catch more FS by increasing the loading affinity. Thus the Raman signal and loading affinity were intensified through the assembly of MB/EV-FS-AgNPs and MB/EV-FS-GO, discretely.

Molecular imprinted polymers (MIP) have been used for PFAS identification, due to the target molecule-imprinted nano-cavity created during the polymerisation process. For example, Li et al. (2014) developed a method in combination of TiO₂ nanotube arrays with MIP for the analysis of PFOA, PFOS and PFHA, in tap, river and mountain waters. It resulted in a LOD of 86 ng/L (ppt). Fang et al. (2016a) also introduced this method for the analysis of PFOS, PFOA and 1H, 1H, 2H, 2H-perfluorooctanesulfonic acid (6:2 FTS) in AFFFs solution. Pencil lead was used as an electrode surface and polypyrrole (PPY) was coated on it, and methylene blue (MB) was introduced to form an AFFF vs. MB ion-pair interaction, which supposedly increased the methods' selectivity.

Another example of MIP is provided by Chen et al. (2015) who developed a specific and sensitive platform and established an electrochemiluminescence (ECL)-based sensor by the modification of a two-dimensional ultrathin nanosheet of carbon nitride (utg-C₃N₄). Based on MIP-SPR (surface Plasmon resonance)-POF (plastic optical fibre), a molecularly imprinted polymer, rather than SAM on AuNP, was used to detect PFOA, PFOS and PFAs in water samples (Cennamo et al., 2018). The method can be used to detect the target pollutants with the LOD of 0.13 ppb to 0.15 ppb.

In addition to NP-based sensors, aggregation-induced emission (AIE) is also receiving increasing attention. In contrast with the traditional aggregation-quenching, these synthesised AIE molecules emit fluorescence once aggregated. Based on this, a glass-chip-AIE-based sensor was introduced by Fang et al. (2019). In this method, AIE luminogens (AIEgen) were added into a solution (water: acetone) containing PFAS. When a droplet was exposed in air for evaporation, different vapour pressures of water and acetone prompted PFAS to reach a critical micelle concentration (CMC) first, then the AIEgen molecules were trapped and aggregated by the hydrophobic core of PFOA micelles. The micelles of PFOA could be turned on by the AIEgen-fluorescence and thus the concentration of analytes was measured under UV illumination (Fig. 4). The method is very simple and can detect PFOA within a short time (~1 min) and with a small amount of sample (1–2 μ L).

3.2. Smartphone app-based sensor

While the above techniques are generally carried out in research laboratories, scientists are also working to develop new systems for real-time monitoring and on-site screening of pollutants. To this end, the smartphone app-based sensor

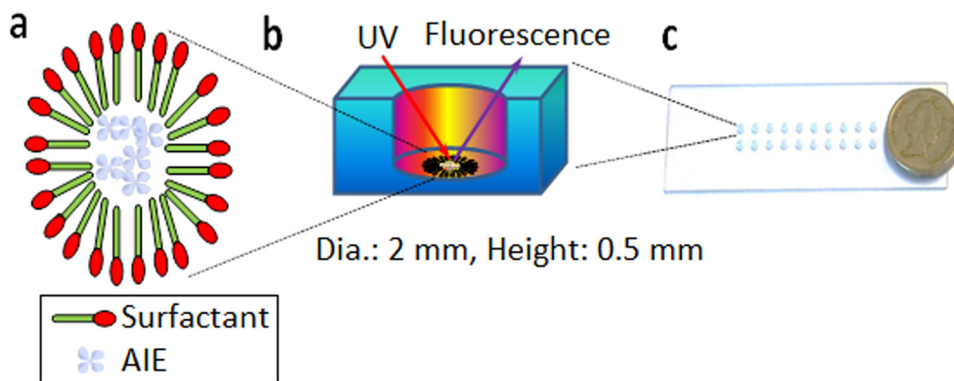


Fig. 4. AIE aggregated by the support of micelle (a), AIE-micelle exists on the bottom of chip-hole (b), A \$2 AUD coin indicates the size of the chip (c).

Source: The Figure was adapted with the permission from Fang et al. (2019).

opens new possibilities for the on-site trace analysis of halogenic compounds (Levin et al., 2016; Sumriddetchkajorn et al., 2013), heavy metals (Wei et al., 2014), pH (Kim et al., 2017; Lopez-Ruiz et al., 2014), biomaterials (Lillehoj et al., 2013), as well as organic and inorganic substances (Fang et al., 2018; Puangpila et al., 2018).

For illustration, an app-based sensor was recently developed by Fang et al. (2018) to sense PFOA in tap water and ground water. Prior to the app sensing, extraction was carried out by adding astkCARE™ reagents (ethyl acetate and ethyl violet) to remove the background, which might be inorganic ions or other components (see Fig. 5).

Typically, when the astkCARE™ reagent is added to a sample containing anionic surfactants (AS) like PFOA/PFOS, the cationic dye such as ethyl violet from the reagent will react with the AS. Therefore, an immiscible ion pair is formed, which is hydrophobic as their hydrophilic terminates are shielded by each other due to an ion-pairing interaction. This ion-pair is extracted from the aqueous phase to the organic phase (Fig. 6). After several steps of extraction, the smartphone's camera reads the colour of this organic phase. An app has developed a link between the colouration (RGB-Red, Green, and Blue) and the concentration of the AS, with a standard deviation of <10% in the range between 10 to 1000 ppb.

The smartphone sensor device is sensitive (detected down to 0.5 ppb, after SPE), and portable. However, it is not highly selective for particular anionic surfactant detection, which will be further improved and enhanced in future research.

4. TOPA and TOF for PFAS and precursors analysis

4.1. Total oxidisable precursors assay (TOPA)

Some PFAS, such as perfluoroalkyl acids (PFAAs; i.e., PFCAs and PFSAs) are formed by degradation of precursor molecules. These terminal degradation products are formed when the non-fluorinated domains of the precursor molecules decompose. The total number of PFAS in the global market is estimated to be almost 5000 (FDA, 2019), but most of them (~90%) are categorised as PFAS precursors (Anonymous, 2018). Therefore, it is essential to detect the PFAS precursors in different matrices.

The current detection techniques are only capable of detecting a certain type of PFAS, but not their precursors, either due to the absence of standards or because the structure of the precursor is unknown. To fill this gap, the total oxidisable precursors assay (TOPA) has been introduced to analyse PFAS precursors. In TOPA, excessive amount of oxidant is used to oxidise PFAS precursors under an alkaline environment, to transform or convert the “unknown” PFAS precursors to the detectable PFAS, such as PFCAs (Fig. 6a). The oxidants include hydroxyl radicals ($\cdot\text{OH}$) generated from the thermolysis of strong oxidant, like persulfate ($\text{S}_2\text{O}_8^{2-}$), and $\text{SO}_4^{\cdot-}$; as well. As a result, a quantitative analysis is carried out after TOPA (Fig. 6b and Table 3).

The method was first introduced by Houtz and Sedlak (2012) to detect N-Me-FOSAA (N-methyl fluoroctane sulphonamide), N-Et-FOSAA (N-ethyl fluoroctane sulphonamide) and FOSA (perfluoroctane sulphonamide) precursors in stormwater. An increased concentration of PFCAs (~69%) was observed after TOPA. In the risk assessment and remediation of PFAS, one needs to consider the whole PFAS family, including the PFAS precursors, “knowns” and “unknowns”. Therefore, increasing research efforts have been made to advance the technology of TOPA thereafter, to cover PFAS and precursors.

Increased levels of target PFAS were identified in samples collected from heavily contaminated zones using TOPA (Houtz et al., 2013; McGuire et al., 2014). Houtz et al. (2016) also applied TOPA to measure various types of precursors from a waste water treatment plant (WWTP) and a firefighting zone. They found that the total concentrations of target PFAS increased to 33%–63% by TOPA. When TOPA was also applied in river and WWTP effluents, an increased amount of PFAS (28% vs. 69%) (mass balance) was also reported after TOPA (Ye et al., 2014).

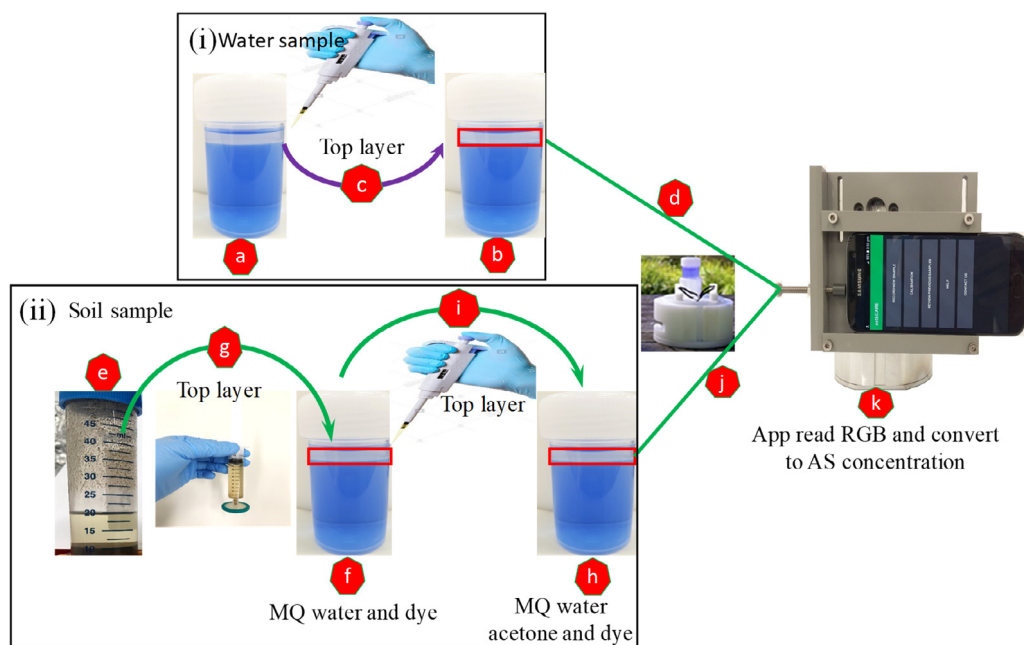


Fig. 5. Smartphone app-based sensor, developed in authors' lab. PFAS are analysed with app based reading kit (k), after dual-(i, for water sample) or tri-extraction (ii, for soil sample). Briefly, during the extraction process, anionic surfactant (AS, i.e., PFOA/PFOS) reacts with cationic dye (i.e., ethyl violet-EV) to form ion pair (a, e, f). Then, this ion pair is extracted into the organic phase (usually the top layer) and transferred (c, g, i) to next container (b, f, h) to read the concentration of AS with the smartphone app-based sensor (d, j, k). Meanwhile, background interference from inorganic salt/ions is removed by using MQ water in the first (a, e), second (f) and third container (h) of dual- and tri-extraction methods, respectively.

Recently, TOPA was applied for soil analysis. The polyfluoroalkyl phosphoric acid esters (PAPs) and bis-[2-(N-ethyl perfluorooctane-1-sulfonamido) ethyl] phosphoric acid ester (diSAMPAP) were transformed to PFCAs (TFAA, PEFrA) (Janda et al., 2019b).

TOPA is an easy and simple way to quantify the mass balance of known and unknown PFAS precursors, but more work is needed to generalise this process. In the near future, TOPA could be applied for the assessing of fate and transport of PFAS from different segment of environmental matrices, which is still a research gap at this moment.

4.2. Total organic fluorine (TOF) and total fluorine (TF)

PFAS and PFAS precursors may exist in trace concentrations in environmental matrices, which leads to an analysis challenge. This challenge is even more serious when the precursors are unknown, either because of the commercial reasons, or due to the partial degradation as intermediates, or owing to the unavailability of their standards for quantification. Consequently, new methods have been introduced to detect fluorinated substances, such as through the total organic fluorine (TOF) analysis (or assay) (Table 4). Typically, methods for TF (organic and inorganic) analysis include particle-induced gamma-ray emission (PIGE), absorbable organic fluorine (AOF) and combustion ion chromatography (CIC). Recently, fluorine-19 nuclear magnetic resonance spectroscopy (^{19}F -NMR) (Okaru et al., 2017), inductively coupled plasma-mass spectrometry (ICP-MS/MS) (Guo et al., 2017), X-ray photoelectron spectroscopy (XPS) (Boča et al., 2012) have also been developed for fluorine/organic fluorine detection.

The PIGE method can quickly measure TOF, once PFAS are separated from the background, such as by SPE. That is, TOF depends on the sample preparation. When extractable fluorinated substances are adsorbed by adsorbent materials, TOF is subsequently detected (Ateia et al., 2019; Wagner et al., 2013). CIC involves the adsorption of PFAS including their precursors on an activated carbon matrix (ACM), which is then combusted and the released fluorine from the PFAS is measured. Both of these methods are capable of measuring TOF at ultra-trace levels, to check the mass balance, but could not trace individual components presented in the samples (Ateia et al., 2019).

The PIGE method uses an ion beam to determine TF in textile and paper components (Ritter et al., 2017). The method demonstrates it is rapid and useful for quantitative analysis, but the requirement of nuclear excitation (gamma-ray) adds complexity and expense.

Table 3
Analysis of precursors using TOPA in different matrices.

Precursors*	Converted to	TOPA conversion rate (mol%) of precursors into PFCAs (by mole/mass)	Sources	Reference
FOSA, N-EtFOSAA, N-MeFOSAA	PFOA, PFHxA, PFPeA	25–69	Water	Houtz and Sedlak (2012)
6:2 FtS, 8:2 FtS, FHxSA, PFHxSaAm	PFCAs	41–100 23–28	AFFF Groundwater and solid sample	Houtz et al. (2013)
PFCA, PFSA precursors	PFCAs	69	River, sewage treatment plant	Ye et al. (2014)
PFPis, 6:2 FtS, EtFOSAA, 8:2 FtS, MeFOSAA	PFCAs	33–63	Wastewater	Houtz et al. (2016)
Precursors*	Converted to	TOPA conversion rate (mol%) of precursors into PFCAs (by mole/mass)	Sources	Reference
6:2 FTSA, 6:2 FTAB	PFCAs	18–77	River water	Boiteux et al. (2017)
6:6PFPi, FOUEA, 8:2 diPAP, FHUEA, 6:2 FTSA, 6:2 diPAP, SAmPaP	PFCAs	0–45	Textile and paper ingredients	Robel et al. (2017)
6:2 FtS, 8:2 FtS	PFCAs	78	Water and sediment	Weber et al. (2017)
6:2 fluorotelomer precursors	PFCAs	56	Wastewater treatment plant	Houtz et al. (2018)
6:2 FtTAoS	PFCAs	67	AFFF	Yi et al. (2018)
N-MeFOSAA, 8:2 FtS, 6:2 FtS	PFCAs	30–67	Portable reuse system	Glover et al. (2018)
Precursors*	Converted to	TOPA conversion rate (mol%) of precursors into PFCAs (by mole/mass)	Sources	Reference
6:2 FTAB, 4:2 FtS, 6:2 FtS, 8:2 FtS, 10:2 FtS, PFOSAm, FHxSA, 5:3 acid, 7:3 acid, 6:2 FTUCA, 8:2 FTUCA, 10:2 FTUCA, FOSA, MeFOSA, EtFOSA, FOSAA, MeFOSAA, EtFOSAA, PFOAB, PFOSB, PFOANO, PFOSNO, PFOSAmS	PFCAs	61–112	Ground water	Martin et al. (2019)
FEtSA, FBSA, FHxSA, FOSA	PFCAs (TFAA, PFBA, PFHxA, PFOA)	~50	Soil	Janda et al. (2019b)

Table 4
Measurement of fluorine in different matrices using TOF analysis (or assay).

Extraction method	Validated by	LOD (ppb)	Sources	Reference
SPE	LC-MS/MS	–	Seawater	Miyake et al. (2007a)
IPE	CIC	3.00	Human bloods	Miyake et al. (2007b)
Solvent extraction	GC	0.043 (MDL)	Model compound	Koc et al. (2011)
Solvent extraction	CIC	–	Soil	Wang et al. (2013)
SPE	CIC	1.00	Waste, surface, ground and drinking water	Wagner et al. (2013)
–	CIC	0.77	Municipal effluent, river and ground water	Willach et al. (2016)
SPE	PIGE	2.00–15.00	Textile and paper	Ritter et al. (2017)
SPE	CIC	–	AFFFs	D'Agostino and Mabury (2017)
–	HR-CS-MAS	0.00028	Fish and seafood	Ozbek and Akman (2018)
Solvent extraction	CIC+ PIGE+ INAA	–	Food ingredients	Schultes et al. (2019)

Recently, TF and extractable organic fluorine (EOF) were determined in food packaging material with several methods, namely CIC, PIGE, instrumental neutron activation analysis (INAA) (Schultes et al., 2019) etc. Among them, CIC showed good accuracy and recovery with the lowest LOD, compared to the other techniques. Consequently, CIC is receiving increasing attention.

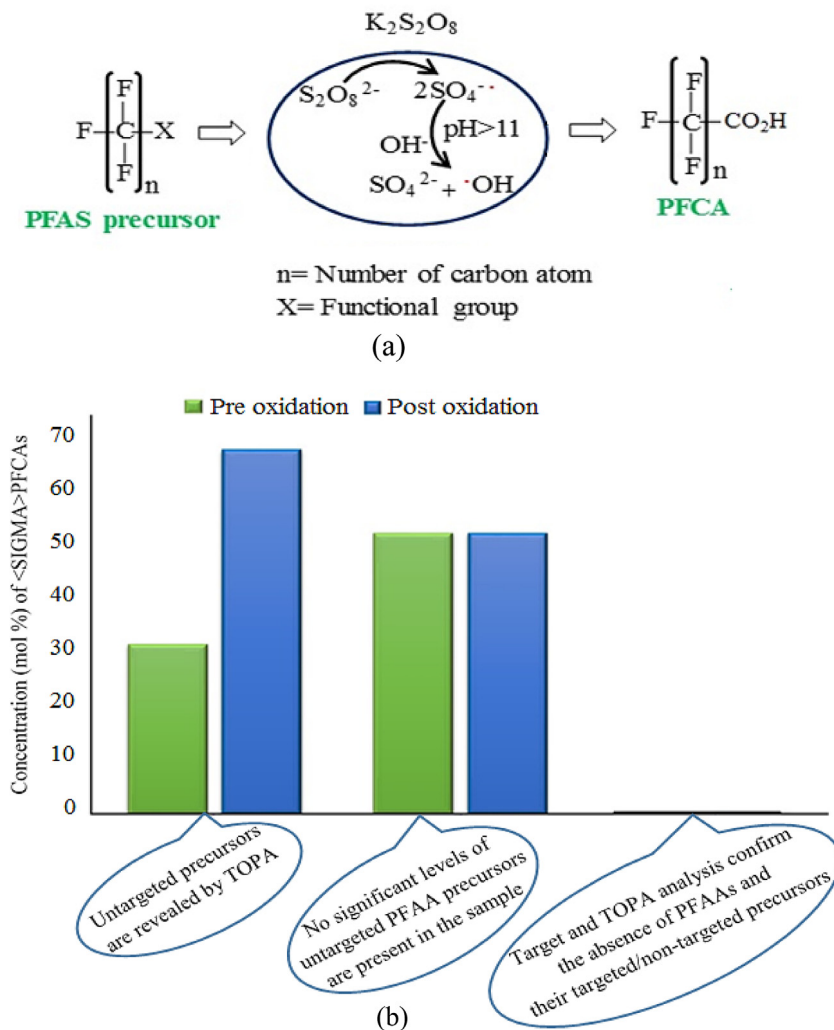


Fig. 6. Schematic drawing of total oxidisable precursors assay (TOPA) protocols (a). Generally, predicted TOPA results are shown graphically before and after oxidation (b), according to the TOPA based published work, from 2012 to 2019.

The TOF was applied to detect organic and inorganic fluoride from seawater and blood samples (Miyake et al., 2007a,b). Extraction was done on SPE and IPE with methyl *tert*-butyl ether (MTBE) and hexane. After SPE, PFAS including precursors were determined by the CIC.

Wagner et al. (2013) applied a modified CIC method for the determination of AOF in several aqueous matrices. In this case, an ACM was used to adsorb PFAS and their precursors, then organofluorine was measured through CIC. This method can detect ~40% to 50% (mass balance) of fluorine, but adsorbent selection and removal of inorganic material from the fluorine content are complex (D'Agostino and Mabury, 2017).

Furthermore, TF might be different from TOF. For example, TF was detected in seafood and fish samples, measured by molecular absorption of calcium monofluoride (CaF) (Ozbek and Akman, 2018). After filleting and chopping, samples were kept at 110 °C for drying and pyrolysis at 900 °C in a graphite furnace. Then TF was measured by high-resolution continuum source-molecular absorption spectrometry. However, a brief scenario of analytical techniques in determining total fluorine content in various biological matrices such as blood, plasma, serum, urine and saliva were concisely presented by Belisle and Hagen (1978).

5. Conclusion

Environmental matrices are frequently contaminated by the various types of PFAS including precursors, their monitoring is vital to facilitate remediation efforts. Considering their low levels in the environment, sample preparation has been developed to extract PFAS, including precursors and short chain of PFAS. LC-MS/MS with negative electrospray ionisation

(-ESI) mode is the most common and trustworthy analytical tool for the selective and sensitive analysis of ionic, anionic and neutral PFAS, while GC-MS is mainly applied for volatile PFAS analysis. To enable on-site analysis by pre-screening, a nanoparticle-based sensing platform has been developed to detect PFAS.

We recommend several research gaps to be filled in the near future, including

- (i) PFAS sampling and preparation towards the analysis of the whole family of PFAS and PFAS precursors.
- (ii) TOF analysis for greater coverage of PFAS precursors and short chain of PFAS. In the meantime, total organic fluorine (TOF) and total fluorine (TF) are analysed by applying PIGE, CIC, 19 F-NMR, ICP-MS/MS) and XPS detection techniques.
- (iii) For on-site analysis or pre-screening, sensitivity and selectivity might be sacrificed to achieve a quick response. For example, an app-based test with dual-/tri- liquid-liquid extraction method could be easy and convenient for field application, as all the procedures (i.e., sample preparation, monitoring and analysis of sample) can be completed in a single response.
In case of sensor development, interference originating from potential cross reactivity should be considered to avoid false results. The challenges for the detection of mixed PFAS in environmental and biological matrices, and in the presence non-PFAS surfactants should also be addressed.
- (iv) The chemistry of PFAS and their precursors are sometime unknown, complex and uncertain. Therefore, some challenges might arise during their analysis, thus efforts are need to overcome their limitations.

By addressing these challenges, monitoring and analysis of PFAS from different environmental matrices will be faster and more general.

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.

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