Article

Evaluation of Pure PFAS Decrease in Controlled Settings

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ABSTRACT: Since 1940, poly- or perfluorinated alkyl substances (PFAS) have been largely used in many applications, including paints, fire foaming, household items, product packaging, and fabrics. Because of their extremely high persistency, they have been defined as "forever chemicals". Although the EU is taking action to reduce their use, their widespread occurrence in environmental matrices and their harmful effects on human health require the use of highly performing analytical methods for efficient monitoring. Furthermore, novel PFAS are constantly revealed by both EU and National environmental agencies. The objective of this work is to investigate the cause of the signal decrease during the analysis of a standard PFAS mixture in water-based matrices, by proposing an efficient technical procedure for laboratory specialists. The analyses were carried out on a mixture of 30 PFAS, including both regulated and unknown substances (which are expected to be introduced in the guidelines), characterized by different chemical features, using LC-vials of two different materials, namely, glass and polypropylene, and dissolved in two solvents, namely, water and water−methanol. The temperature of analysis and the concentration of PFAS were also considered through LC-MS analyses at different times, in the 0−15 h range. Depending on the chemical structure and length of the PFAS, sampling and treatment procedures may be adopted to tackle the decrease and the release from the containers, reducing the risk of underestimating PFAS also in real water matrices.

KEYWORDS: PFAS, mass spectrometry, adsorption, drinking water, containers
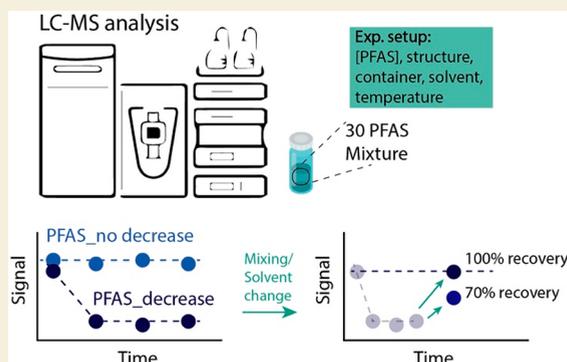
INTRODUCTION

Poly- or perfluorinated alkyl substances (PFAS) are a class of compounds of more than ten thousand chemicals, consisting of a partially or fully fluorinated hydrophobic alkyl chain with varying length and a functional group, usually hydrophilic.[1] These substances have long been used in a wide range of industrial and commercial applications (e.g., Teflon, Scotchgard, food packaging, cosmetics, waterproof textiles, etc.).[2] However, due to their extreme persistence and high chemical stability, they are now widespread everywhere, becoming known as "forever chemicals".[3−5] As mentioned above, PFAS encompass thousands of chemicals, but environmental studies have primarily focused on perfluoroalkylsulfonic acids (PFSA), such as the well-known perfluorooctanesulfonic acid (PFOS), and perfluoroalkylcarboxylic acids (PFCA), including perfluorooctanoic acid (PFOA). PFSA and PFCA are low molecular weight surfactants, consisting of homologous series of molecules that differ in the length of the fluorinated alkyl chain (typically C4−C14). Due to their persistency and bioaccumulation, they have been found in water, land, air, food, and even human samples.[6−8] In addition, due to their potential toxicity, regulatory activities at both the national and international levels are increasing along with the development of novel strategies to both detect and treat contaminated matrices. Particularly, the development of novel and accurate analytical procedures for detecting PFAS is of essential

importance in evaluating their transport and fate. Various methods, including chromatography, mass spectrometry, and portable sensors, are currently being developed.[9−12] Although all these approaches are highly efficient and sensitive, PFAS sampling, storage, and analysis continue to represent a challenge.[13−16]

The PROMISCES[17] project, entitled Preventing Recalcitrant Organic Mobile Industrial chemicalS for Circular Economy in the Soil-sediment-water system, intends to identify how industrial pollution prevents the deployment of the circular economy (CE) in the EU and which strategies help overcome key bottlenecks to deliver the ambitions of the European Green Deal and Circular Economy Action Plan. As a consequence of this, new analytical methods and toxicological tools are required to provide data on persistent mobile substances (i.e., PFAS and other industrial chemicals) in complex environmental matrices released from (i) soil, (ii) sediment, (iii) landfills, and (iv) wastewater treatment plants and (v) via urban runoff into relevant environmental

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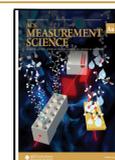
compartments. As part of this project, the development and validation of analytical methods for detecting and quantifying selected PFAS compounds in reverse osmosis and nanofiltration concentrates, leachates, sewage sludges, and contaminated sediments are included. As established by analytical guidelines, PFAS protocols developed by the EPA, ASTM, and others recommend the use of polypropylene containers for storage and analysis (including LC vials) and avoidance of contact between samples and glass surfaces.[18] In particular, as reported in EPA 8327, one of the official LC-MS/MS standard protocols for analyzing PFAS in surface water, groundwater, and wastewater matrices, the loss of PFAS was observed during the storage of standard solutions in 50% methanol using glass containers. To prevent undesired decreases in PFAS concentration, the use of polypropylene (PP) and high-density polypropylene (HDPP) containers is recommended.[19] However, in a recent work, authors showed that the behavior of the adsorption of perfluorooctanoic acid (PFOA) to various containers is lower on glass than on polypropylene, respectively, 14−23% and 32−42%.[20] Moreover, this phenomenon was observed in long-time experiments for PFAS remediation in real water samples, demonstrating that salts can significantly increase the adsorption.[21] Also, it should be considered that the presence of long carbon chains has a relevant effect on the adsorption on the wall of containers, e.g., glass, polypropylene, and the presence of nonaqueous solvent might avoid this issue.[22] However, the adoption of high-content of organic solvents to conduct analysis is not always practicable even considering some studies focused on toxicity of these species.[23,24] The topic is of high interest, and various studies have been reported in the literature, considering the known PFAS of main interest.[25−27] In addition to the containers and the solvents used for sampling and storage, temperature and time seem to have a role as indicated by the established guidelines of the EPA.[28] However, it should be noted that a unique consensus is still missing and the list of PFAS and related-species is increasing; thus, new procedures will need to be developed.[29] In this work, we applied an accredited LC/MS/MS method, based on EPA 533 and EPA 537.1, for the analysis of 30 PFAS, including both perfluoroalkyl sulfonic (PFSA) and carboxyl compounds (PFCA). All the analyses have been carried out while considering different vials materials (glass and polypropylene), solvents (water and water−methanol), and temperature conditions (15 and 25 °C), factors that may affect PFAS behavior and which are more frequently selected by accredited laboratories for PFAS analysis. Samples were freshly prepared directly in the designated LC vials, all the same geometrical shape, and analyzed over a duration of 15 h. Adopting a systematic approach, all PFAS have been kinetically characterized in order to understand how different experimental conditions may affect their availability by avoiding false negative results during measurements. In addition, these kinetic studies provided preliminary data on the different analyzed species, which are strictly dependent on their chemical structures, allowing for the development of more efficient analytical protocols for PFAS storage and analysis. This article could represent a starting point toward the development of analytical methods also for emergent PFAS, expected to be introduced in the official methods (i.e., EPA, EU, nationals) as recommended in the PROMISCES project objectives.

■ MATERIALS AND METHODS

Reagents and Instruments

Optima LC-MS grade acetonitrile, ultrapure water, and methanol were purchased from Biosolve. LC-MS grade (>99%) ammonium acetate was purchased from VWR. Vials (Phenomenex: part no. AR0-3611-12) were purchased by Phenomenex. Certified Standards list: PFAS (C4−C10 mixture) ES-5576 brand CIL, PFCA (C4−C14 mixture) ES-5587 brand CIL, Standard PFAS Mixture (7 components), and C6O4 difluoro((2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl)oxy)acetic acid (purchasing procedure with permission, certificate not available) were purchased from Ultra Scientific (CAS single analytes 757124-72-4,27619-97-2, 39108-34-4, 2991-50-6, 754-91-6, 13252-13-6, 2355-31-9); L-PFUdS 441296-91-9, L-PFDoS 1260224-54-1, L-PFTrDS 174675-49-1, NaDONA 2250081-67-3 and MPFAC-24-ES mixture were purchased by Wellington Lab. Except for MPFAC-24-ES (solvent Methanol/Isopropanol 2%/water 1%), all other standards listed are in methanol. All solvents and consumables were monitored for PFAS contamination in each new lot used.

The UHPLC-MS/MS instrument setup comprises a Thermo Scientific UHPLC UltiMate 3000 system equipped with pumps, a refrigerated autosampler, a thermostated column compartment, and a degasser. It is coupled with a Thermo Scientific TSQ Altis triple quadrupole mass spectrometer featuring an ESI source. The chromatographic column used is a Luna Omega 1.6 μm PS C18 100 Å, with dimensions of 100 × 2.1 mm, from Phenomenex or an equivalent. The delay column employed is a Luna 5 μm C18(2) 100 Å, sized at 30 × 3 mm (Phenomenex; Part No: 00A-4252-Y0). For LC-MS analysis, two distinct mobile phases were chosen: mobile phase A consists of water with 5 mM ammonium acetate, while mobile Phase B is composed of acetonitrile (all the instrumental and experimental conditions are carefully described in the Supporting Information file, Tables S1−S3).

Experimental Setup

Four vials were prepared for each experiment and shaken manually (we observed that the use of vortex systems might facilitate the adhesion of the PFAS on the surface of the containers). All the solutions have been prepared using both different solvents and containers, specifically: 200 ng/L in polypropylene vials using water as the solvent, 200 ng/L in polypropylene vial using water−methanol 70:30 as the solvent, 200 ng/L in glass vials using water as the solvent, and 200 ng/L in glass vial using water−methanol 70:30 as the solvent. The same experiments have also been performed using a higher concentration of PFAS, namely, 1 μg/L, and the autosampler temperature was set up at 15 and 25 °C. To obtain a kinetic profile of measurements, each solution was analyzed at various times, including 0, 3, 6, 9, 12, and 15 h, as schematized in Figure 1.

All vials tested have the same surface area. A delay column was employed to prevent PFAS release from the instrument. Additionally, in order to assess the potential presence of PFAS in the working materials and in the UPLC system (in particular PTFE), a background signal was recorded before each analytical session. According to the EPA guidelines for PFAS analysis, the background signal should be smaller of 1/3 of the LOQ (Limit of Quantification). In our case, all the analytes in water and in water−methanol present a background concentration of zero or at most <5 ng/L, which is 40 and 200 times lower than the concentrations we are analyzing (200 ng/L and 1 μg/L, respectively) and all cases lower of our LOQ (15 ng/L).

■ RESULTS AND DISCUSSION

The rationale of the proposed study was focused on providing significant indications on how to handle PFAS compounds during their sampling and quantification. PFAS are generally adsorbed on containers, causing a major source of error in both the sampling and analysis phases. Although the EPA and other agencies mainly suggest the use of PP containers, the debate is
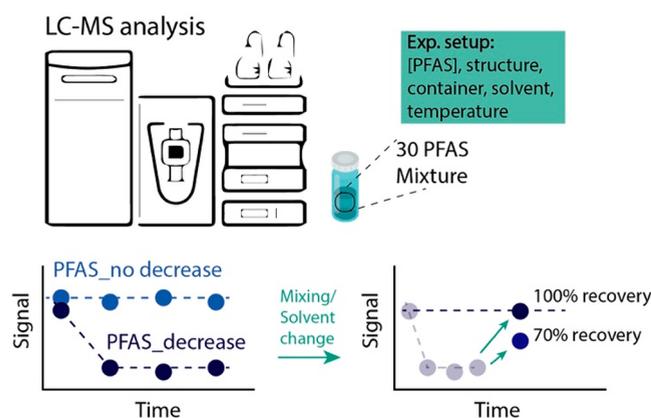
Figure 1. Schematic representation of the LC-MS workflow to evaluate decrease of signal during 15 h PFAS analysis, and treatment to reduce adsorption phenomena that depends on the specific structure of PFAS, the container, and the solvent.

still ongoing, and data for justification are scarce. Since the chemical composition of PFAS, their concentration, the analytical temperature, the storing/working solvent and the containers represent important variables to be considered, all the measurements have been performed using a validated LC-MS method on a mixture of 30 PFAS. In order to have a clearer discussion of the results, the list of analyzed PFAS have been classified under five groups depending on the occurring similarities of their structures, as reported in following Table 1.

Table 1. PFAS "Classification" Depending on Composition/Structure

PFAS "classification"	list of analyzed
sulfonates	PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFUdS, PFDoS, PFTrS
carboxylic acid	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA, PFTeDA
telomer	4-2 FTS, 6-2 FTS, 8-2 FTS
sulfonamides	FOSA, N-MeFOSAA, N-EtFOSAA
C—O—C	GENX, NaDONA, C6O4

As described in Experimental Setup, all the analyses have been carried out varying different factors (e.g., temperature, solvents, containers, and concentration). The changing in PFAS signal over 15 h analysis has been reported in the Supporting Information file (SI), Figures S1−S20. After having carefully observed all the signal variation for the species involved in the study, although some differences appeared, three major groups might be identified with respect to the variation of quantitation MS peaks in the 0−15 h range: Group I (no variation), Group II (baseline variation), and Group III (decrease with time), as reported in Table 2.

With regard to Group I, which includes the majority of PFAS that have been analyzed, the behavior reported in Figure 2A is consistent with similar MS areas at both the starting time and end time (15 h), highlighting how the choice of solvent, container, concentration, and temperature does not cover a major role in the adsorption process, as shown for NaDONA.

With regard to PFAS analyzed and inserted in Group II, the occurrence of a different baseline was observed, even if the signal did not show significant variation over the analytical section, as shown in Figure 2B. For all the concentrations and

Table 2. PFAS "Classification" Depending on the Variation of the Area of the Product (Expressed as Counts·min) Calculated in the 0−15 h Range

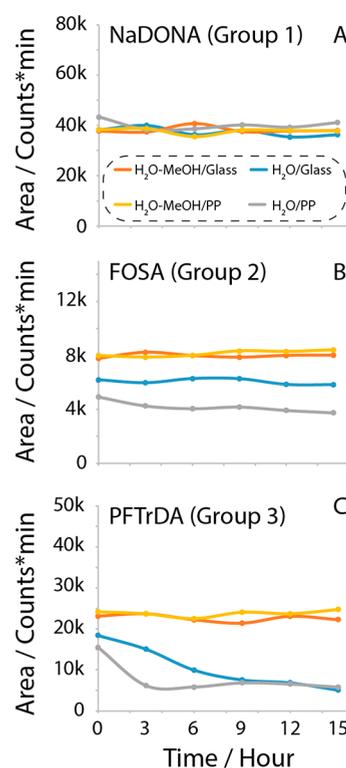| PFAS "classification"	list of analyzed
Group I	PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUdA, GENX, NaDONA, C6O4, 4-2 FTS, 6-2 FTS, 8-2 FTS, N-MeFOSAA
Group II	PFDoA, PFDS, FOSA, N-EtFOSAA.
Group III	PFTrDA, PFTeDA, PFUdS, PFDoS, PFTrS.

Figure 2. Evaluation of quantitation MS peak of 1 μg/L (A) NaDONA, (B) FOSA, and (C) PFTrDA. All the LC-MS experiments have been conducted using a temperature of 25 °C up to 15 h. The experimental setup is represented by two types of containers, i.e., glass and PP, and by two solvents, i.e., water and water−methanol, as reported in the inset of Figure 2A.

temperatures that have been considered in the study, the measurements carried out in the water−methanol mixture were characterized by the highest MS quantitation peaks as highlighted for FOSA. As confirmed in a recent study,[29] in these cases the behavior might be attributed to the increased percentage of methanol with respect to the other measurements that have been carried out in water, which show a low signal at the starting point of the measurements without any significant decrease during the 15 h. With regard to Group III, the typical behavior is shown in Figure 2C. These measurements are characterized both by the presence of a different baseline and the presence of a signal decrease during time. With regards to the former, it can be observed how the starting values are lower when water is used as the solvent, indicating the existence of a solvent-effect on the solubilization of PFAS. With regards the latter, the different container that has been used seems to be responsible of a different interaction with the PFAS in solution, and it is demonstrated by the variation of

Table 3. Percentage of Recovery of PFAS (Group 3) $\pm$ Standard Deviation (n = 3) in Water Using Glass and PP as the Containers

condition/PFAS	PFTrDA	PFTeDA	PFUdS	PFDoS	PFTrS
3 h H$_2$O/glass	82% ± 10%	80% ± 10%	85% ± 3%	83% ± 5%	84% ± 3%
3 h H$_2$O/PP	40% ± 5%	20% ± 8%	58% ± 1%	28% ± 17%	30% ± 22%
15 h H$_2$O/glass	27% ± 1%	16% ± 3%	42% ± 6%	19% ± 4%	25% ± 5%
15 h H$_2$O/PP	31% ± 1%	20% ± 5%	43% ± 7%	28% ± 3%	17% ± 5%

Table 4. Percentage of Recovery $\pm$ Standard Deviation (n = 3) of PFAS (Group 3) after Mixing the Containers

condition/PFAS	PFTrDA	PFTeDA	PFUdS	PFDoS	PFTrS
mixing H$_2$O/glass	81% ± 5%	47% ± 3%	99% ± 3%	52% ± 3%	44% ± 1%
mixing H$_2$O-MeOH/glass	98% ± 7%	93% ± 8%	97% ± 8%	102% ± 15%	100% ± 8%
mixing H$_2$O/PP	64% ± 3%	28% ± 3%	76% ± 5%	42% ± 3%	20% ± 3%
mixing H$_2$O-MeOH/PP	104% ± 8%	88% ± 7%	100% ± 3%	87% ± 3%	69% ± 15%
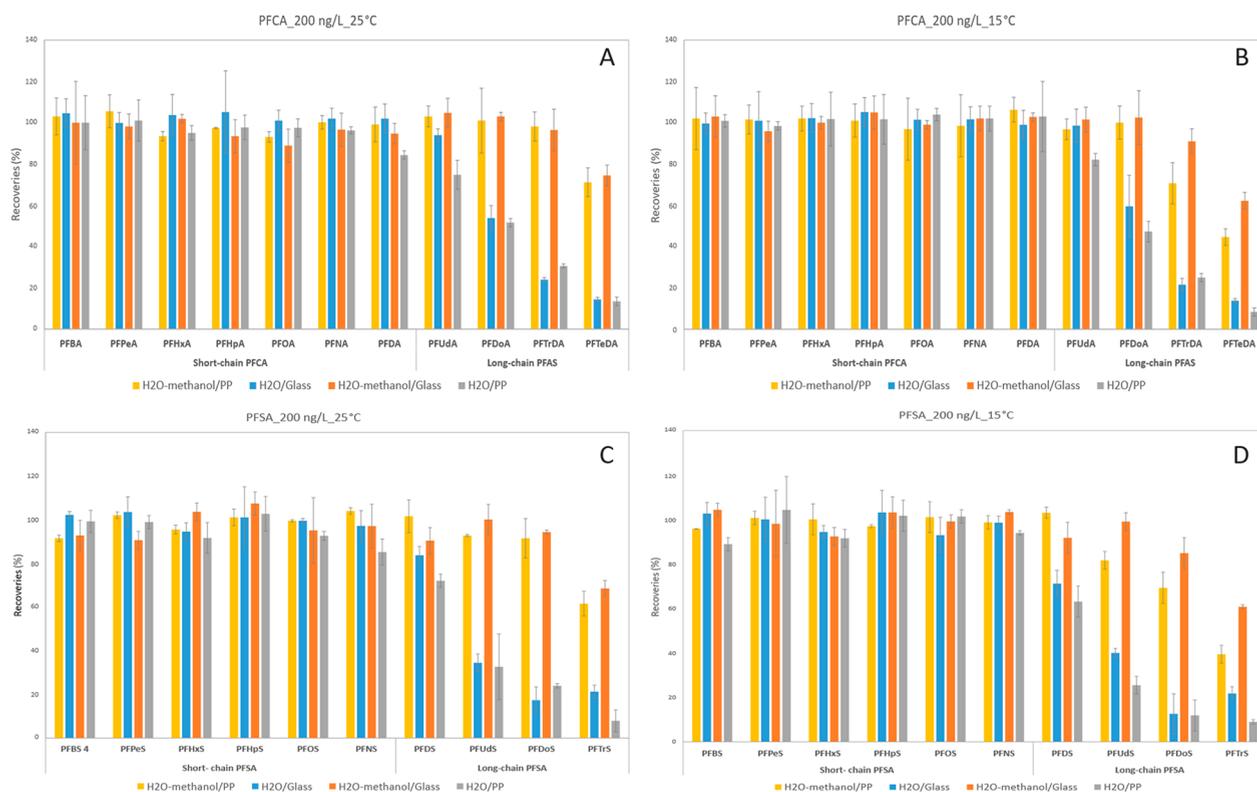
Figure 3. Percentage recoveries (R%) for PFAS mixture in a concentration of 200 ng/L using temperatures of 25 °C (A) and 15 °C (B) for PFCA and 25 °C (C) and 15 °C (D) for PFSA.

signal in the range of time investigated. In addition to this, for all the PFAS that showed this behavior, the decrease of signal is faster when the measurement is carried using water as the solvent and PP as the container, reaching the lowest signal after the first 3 h and remaining constant for the rest of the experiment. This behavior has been observed for all the PFAS that have been inserted in Group III, and for all the concentration and temperature tested. Table 3 displays the signal percentage of recovery that has been observed using 1 μg/L PFAS at 25 °C.

Table 3 displays the variation of MS peak areas after 3 and 15 h, by measuring the listed PFAS at 1 μg/L levels. The percentage of recovery (R%) has been calculated by using the following formula: (S_{tx}/S_{t0}) × 100, where S_{t0} represents the MS quantitation peak at time 0 (reference time before starting analysis) and S_{tx} represents the MS quantitation peak measured

after a fixed time of interest during experiment (Table 3 has been obtained using t_3 and t_{15}, respectively, for 3 and 15 h). As observed, when the PFAS were analyzed in PP, the R% rapidly reached the lowest value (already after 3 h), while the presence of glass container showed a slower adsorption process, demonstrating an active role of the container's material toward the adsorption process. The same experiments have been also carried out using water−methanol as the working solvent, highlighting how this system was characterized by a good R% for all the 30 PFAS in glass containers, never lower than 84%. In PP containers, the system was characterized by a good R% for all the PFAS except for PFTrS (69%). Moreover, the strength of the adsorption phenomena has been also confirmed by adding a manually mixing step of the different solutions after the end point of the study, namely 15 h, by measuring the
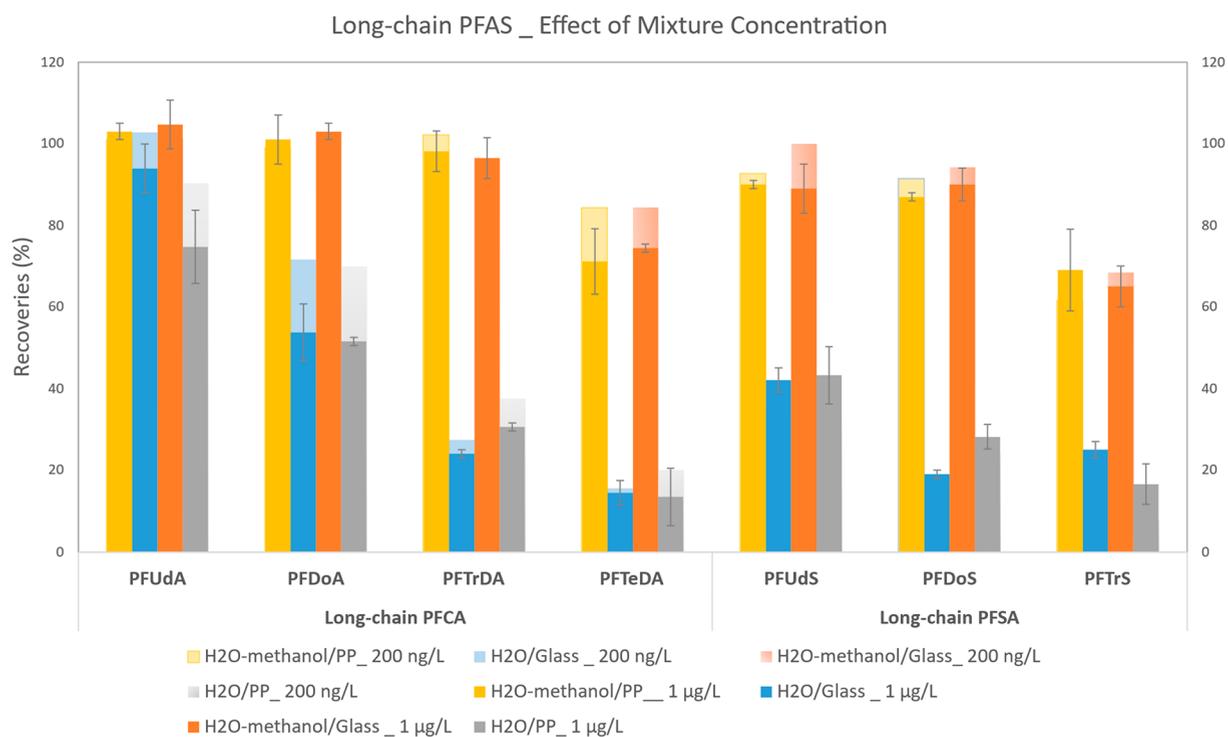
Figure 4. Effect of mixture concentration on percentage recoveries of long-chain PFAS.

percentage of recovery (R%). The results are reported in Table 4.

$R\%$ has been calculated by using the following relationship, $(S_{tmix}/S_{t0}) \times 100$, where S_{tmix} represents the MS quantitation peak measured following a manual shaking of the containers. The results highlight how the only way to obtain a quantitative recovery is represented by the use of glass containers and a water−methanol mixture as the solvent. In addition, it should be noted that the chemical structure of the involved PFAS (especially the length of the chain) strongly affects the calculated value of $R\%$ (Table 4). In fact, what is observed is the following: after the final mixing step, the $R\%$ calculated for PFTrDA is higher than that for PFTeDA (PFCA); the R% calculated for PFUdS is higher than that for PFDoS and PFTrS (PFSA).

To investigate the contribution of hydrophobicity to the surficial bindings to containers, the percentages of recovery (R %) of perfluorosulfonic (PFSC) and perfluorocarboxylic acids (PFCA) have been reported as a function of carbon chain length, as calculated in previous works.[29] The graphs were constructed using two sets of data collected at different temperatures (25 and 15 °C) for the lower concentration of PFAS mixture (200 ng/L), as shown in Figure 3.

Observations reveal that the adsorption of PFAS to the containers increases for long-chain compounds (>10 carbon atoms), resulting in smaller R% values. Overall, the data confirm a higher adsorption in water, as it promotes hydrophobic interactions.[30]

Regarding the choice of both containers and solvents, it is very important to consider the structure of the working material. As discussed, like other mineral surfaces, the main mechanism through which hydrophobic silica acquires a charge is through reaction with H^+ and OH^- ions present in the aqueous solution.[30] The isoelectric point of silica is at pH 2, so for higher pH values, as in this case, it is negatively charged.

PFAS have negatively charged head groups; therefore, the Coulombic repulsion between charges should discourage adsorption. Instead, as shown in Figure 3, adsorption occurs. One possible explanation may be related to the solvent effect: perfluoroalkyl compounds are characterized by a fluorinated hydrophobic chain, and thus, they undergo hydrophobic interactions that reduce the high entropy associated with the solvation effect of water. Despite the negative charge, glass is a hydrophobic material capable of binding PFAS. As the chain length increases, the hydrophobicity of PFAS increases, making them less soluble. This increase in hydrophobicity drives the PFAS toward the solid−liquid interface. By aggregating on the surface of silica through their tails, the exposed surface area to water is reduced, and they aggregate with hydrophobic silanol bridges, reorienting themselves in a hairpin-like mechanism.[30,31] As the solubility of PFAS decreases, the PFAS−PFAS affinity increases, promoting the formation of a monolayer and reducing the rate of the dissociative process, which can be neglected.

Regarding the adsorption of PFAS on PP in an aqueous solution, considering the slow percentage of recovery in Table 3, it is easily observed that the process occurs very rapidly. In this case, PP is a more hydrophobic material (contact angle > 90°), and consequently, it is more attractive for long-chain PFAS. As a result, in contrast to what is recommended by official methods, PP containers may not be the best materials for analyses.

In both cases, methanol appears to delay the adsorption of PFAS, with increasing solubility in the organic phase.

Regarding the effect of temperature, it seems to not significantly affect the adsorption, as confirmed by previous studies.[29] Concerning the effect of the mixture's concentration, recoveries appear lower for higher concentrations, as shown in Figure 4, where increased adsorption is mainly observed for PFCA.
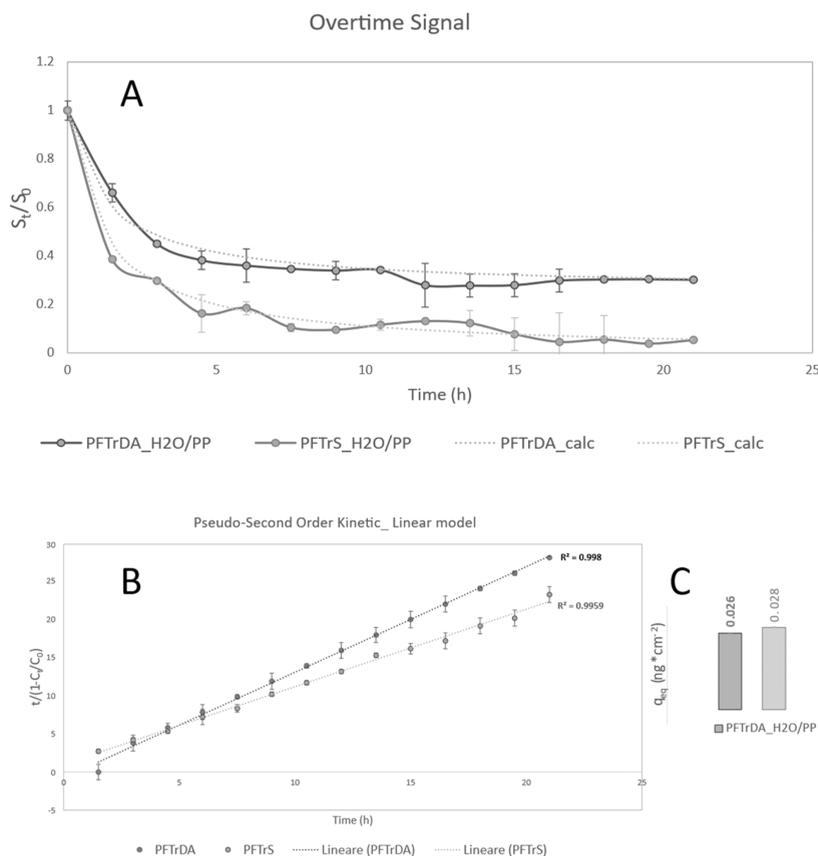
Figure 5. (A) Signal variation overtime (S_t/S_0) recorded in a time range of 0−21 h (±standard deviation (n = 3)) (continuous line) and theoretically calculated kinetic trend (in dots). (B) Linear fit of PFTrDA and PFTrS according to a pseudo-second-order model and (C) sorbate amount per unit surface area (q_{eq}) for each PFAS. Theoretical calculation and fitting were performed through MATLAB version 2022.

In general, it was observed that adsorption is influenced by the functional headgroup, indicating that higher concentrations of sulfonates ($-SO_3-$) were removed from the aqueous phase than carboxylates ($-CO_2-$) with similar chain lengths, probably due to their higher hydrophobicity.

In order to investigate the adsorption mechanism, kinetic data for two PFAS, namely, perfluotridecansulfonic acid (PFTrS) and perfluorotridecanoic acid (PFTrDA), with similar chain lengths but different head groups were recorded at a higher time frequency. For these two PFAS, which appeared to reach equilibrium during the experiment, the adsorbed amount of sorbate q_{eq} (ng/cm^{-2}) at equilibrium was calculated, as reported in Figure 5.

Since the target compounds can only be assessed based on changes in peak areas $\left(\frac{S_t}{S_0} \approx \frac{C_t}{C_0}\right)$, the classical kinetics equation for the pseudo-second-order kinetics (eq 1) was normalized by C_0, where C_0 is the initial concentration (200 ng/L) (eq 2). Subsequently, the ratio $t/(1 - C_t/C_0)$ was plotted against time.

$$\frac{t}{q_t} = \frac{1}{q_{eq}}t + \frac{1}{K_2 q_{eq}^2} \tag{1}$$

$$\frac{t}{1 - \frac{C_t}{C_0}} = \frac{1}{1 - \frac{C_{eq}}{C_0}}t + \frac{1}{\text{constant}} \tag{2}$$

A linear regression was used to fit the plot of $t/(1 - C_t/C_0)$ versus time, finding excellent linearity ($R^2 > 0.99$) as shown in Figure 5B. This demonstrates that PFAS adsorption to PP

follows a pseudo-second-order kinetics, even within a small time window. Therefore q_{eq} was evaluated from the slope and the resulting amount was normalized for the surface area of the vials.[32] (The surface area was calculated as $2\pi r_1 h + 2\pi r_2 l + \pi r_1^2$, where r_1 and r_2 are the diameters of the vial and h and l are the height and the neck height, respectively. In our case, it was found to be 10.78 cm^2.)

The determined amounts of sorbate at equilibrium (0.026 ± 0.002 ng/cm^2 for PFTrDA and 0.028 ± 0.001 ng/cm^2 for PFTrDS) are unexpectedly high, even within a short time window, especially for PFTrS. This confirms the significance of selecting an appropriate container for such studies, taking into account the chemical properties of these molecules.

◼ CONCLUSION

The aim of the present work was to provide an effective method to evaluate the optimal experimental conditions to accurately measure PFAS. To do this, 30 PFAS have been selected and analyzed with a validated LC-MS methodology. The list of analyzed PFAS contains both the ones described by European and National agencies and emergent species. The main aim of the work was to provide laboratory specialists some insights regarding the selection of the proper experimental setup when quantifying PFAS in real matrices. The whole study divided PFAS into three major groups, namely, 1, 2, and 3. In particular, while Groups 1 and 2 were not significantly affected by the choice of container/solvent, PFAS belonging to Group 3 displayed to be strongly dependent on the combination of container and solvent

used. As observed, the utilization of certain solvent/container combinations might result in a loss of PFAS from the working solution, thus yielding an underestimation of the real level, even after shaking the containers. This behavior is strictly dependent on the chemical structure of the PFAS to be quantified; thus, slightly different procedures should be adopted. For instance, the use of PP containers in combination with water as solvent results in a faster adsorption of PFAS with respect to the use of glass containers, most of all for long-chain PFAS. The major affinity of PFAS for PP containers compared to glass is also confirmed by the lower recovery of PFAS after the final mixing step. The results obtained in the presence of a 30% amount of methanol highlighted the decrease of adsorption phenomena and the increase of redissolution using both PP containers (good R%) and glass containers (excellent R%). For the temperature and concentration effects, they seem to slightly affect the percentage recoveries (R%). The high persistence of PFAS, particularly in the environment, makes them a top priority for society as a whole, especially when considering their health effects. Therefore, the primary aim of this study is to shed light on the importance of selecting appropriate containers, temperatures, and solvents. Sampling and treatment are crucial steps that must be carefully considered prior to analysis, and it could be concluded that if only PFAS from Group 1 are analyzed, water samples in both glass and PP can be used as is, while if PFAS from Groups 2 and/or 3 have to be analyzed, the preferred method is to use a 70/30 water–methanol mixture in a glass container.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmeasuresciau.3c00027.

Experimental setup, MS transitions, time analysis during 15 h for all the PFAS and considering concentrations, namely, 200 and 1 μg/L, and temperatures, 15 and 25 °C (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Marco Mancini** conceptualization, data curation, methodology, resources; **Valentina Gioia** conceptualization, data curation, formal analysis; **Alessandro Frugis** resources, writing-review & editing; **Stefano Cinti** conceptualization, data curation, supervision, writing-original draft, writing-review & editing.

Notes

The authors declare no competing financial interest.

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