Laboratory Derived PFAS Interferences from Commonly Encountered Supplies and Equipment Determined Using UHPLC-MS/MS

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Introduction

Per- and polyfluoroalkyl substances (PFAS) comprise a large number of substances that occur in a broad range of applications and products[1]. PFAS are of concern because of their high persistence and impacts on human and environmental health. PFAS pose particular challenges in the analytical laboratory as they are present in common consumables and hardware. EPA Method 533 stipulates laboratories must demonstrate supplies and equipment are not contributing PFAS interference, leading to elevated minimum reporting levels[2]. We present a study of PFAS residues in commonly encountered laboratory supplies and equipment to highlight potential sources of laboratory derived PFAS interferences.

Experimental

32 target analytes including EPA 533 compounds. The target analyte suite contains 10 classes of PFAS, varying by functionality, including carboxylic acids, sulfonic acids and telomers, sulfonamides, and ethoxy compounds.

Reagents

Standards purchased from Toronto Research Chemicals Inc. (Toronto, Canada). Reagents purchased from Merck Life Science UK Limited (Gillingham, UK). LC/MS grade solvents from Rathburn Chemicals Ltd. (Walkerburn, UK). Water (18.2 MΩ.cm) was drawn fresh daily from a Direct-Q 5 water purifier (Merck Life Science UK Limited, Watford, UK).

Sample Preparation

Component Extraction: in triplicate 1/10 (w/v) with methanol, equilibration for 1 hour or ultrasonication for 15 min in polypropylene (PP) centrifuge tubes or polystyrene (PS) universals. Extracts processed alongside a laboratory reagent blank (no evaporation) and an evaporation blank.
Evaporation: Solvent extracts transferred to fresh centrifuge tubes and evaporated using a Turbovap® LV (50 °C, 1.4 to 3.2 L min^{-1} for 40-60 min) supplied with N_2 from a Solaris nitrogen generator (Peak Scientific, Inchinnan UK) serviced from in-house compressed air.
Post extraction: Extracts were either directly injected, diluted prior to injection or evaporated and reconstituted in 50% MeOH (aq).

LC/MS Conditions

Instrument: Shimadzu Nexera UHPLC using fluoropolymer free tubing and a pre-injector trap column (***Figure 1***) coupled to an AB Sciex 5500 triple quadrupole MS system.

Column: Avantor ACE Ultracore SuperC18 2.5 µm (50 x 2.1 mm)
Mobile Phase: A: 5 mM ammonium acetate (aq)
Mobile Phase B: methanol (MeOH)
Injection volume: 10 µL
Flow rate: 0.4 mL min^{-1}
Gradient: 30% B to 95% B (0.1 min to 6.5 min)

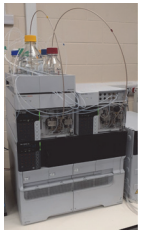

Figure 1. *Nexera UHPLC with reduced PFAS tubing.*

Source parameters (TurboIonspray):
IS: -3500 V **TEM:** 500 °C
CUR: 40 psi **GS1:** 40 psi **GS2:** 60 psi

MRM transitions: Optimized MRM transitions were selected using the most intense precursor ions in negative ionization mode, available on request.

Quantitation: External calibration based on area vs concentration from 8 to 40 ng L^{-1}. Calibration curves were linear over the range, unweighted and forced through the origin.

Results

Blanks and Solvents

The majority of individual PFAS residues from evaporation blanks were estimated below 1 ng L^{-1} and typically below 0.1 ng L^{-1} or the limit of quantitation (LOQ).

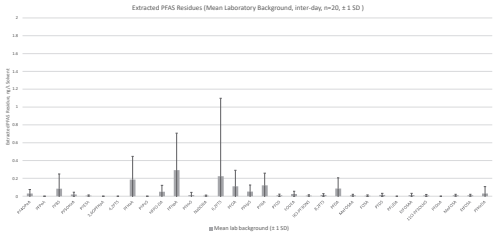

Figure 2. *Inter-day Lab Background, ng L^{-1} extracted (mean ± 1 SD).*

Figure 2 demonstrates laboratory evaporation can be a significant source of measurement uncertainty, procedures should be in place to reduce the incidence of high individual residues that need reanalysis.

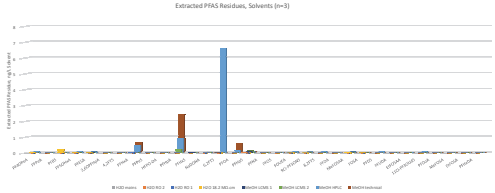

Figure 3. *Laboratory Solvent Residues, ng L^{-1} extracted.*

Solvents used in the analytical laboratory can be a significant contributor of PFAS residue (***Figure 3***). LC-MS grade solvents demonstrate low residues whereas technical and HPLC solvents can contribute individual compounds. Sources of water used in our Cardiff laboratory (including mains water) demonstrated extremely low residues, this may not be the case dependent on supply and service status of RO and purifier system used.

Surface Materials

Choice of materials used in the laboratory can be a source of PFAS residues. Three material surfaces were extracted with a known volume of solvent. ***Figure 4*** demonstrates PP materials have minimal residues. PP residues increase when heat treated at 50 °C for 48 h, this may be due to increased residue transfer from the local environment. Stainless steel (SS) and glass surfaces demonstrate increased residues compared to PP, contact should be avoided unless proven to be residue free by suitable validation.

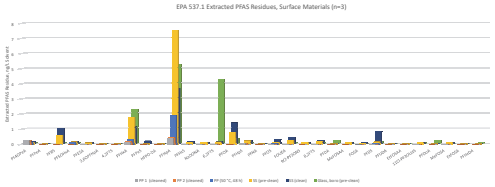

Figure 4. *Laboratory Surface Material Residues, ng L^{-1} extracted.*

Common single use plastic consumables demonstrate low PFAS residues consistent with the lab background, typically estimated below 1 ng L^{-1} (***Figure 5***). Some variation in residue was demonstrated dependent on supplier/manufacturer. ***Figure 5*** appears to demonstrate heat reduces residues when compared to storage at room temperature, contrary to the data in **Figure 4**.

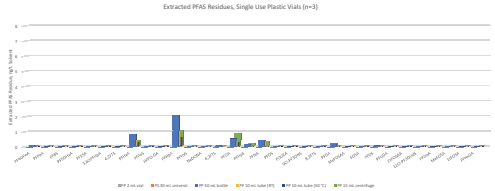

Figure 5. *Single use Plastic Residues, ng L^{-1} extracted.*

Large volume storage bottles can contain significant PFAS residues dependent on construction material (***Figure 6***). Glass bottles are well known for their potential to adsorb PFAS compounds, our data confirm the advice in EPA 533 to avoid contact with glass[2]. High density polyethylene (HDPE) may be a suitable alternative to PP dependent on supplier/manufacturer.

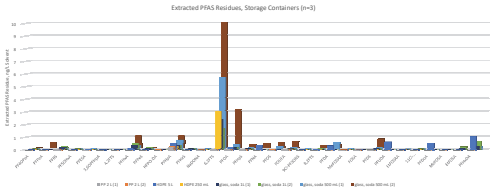

Figure 6. *Storage Bottle Residues, ng L^{-1} extracted.*

Disposable pipette tips used in our Cardiff laboratory are from commonly available sources and manufactured from PP or HDPE. Most pipette tips demonstrate low PFAS residues consistent with the lab background (***Figure 7***). The majority of residues were estimated below 1 ng L^{-1}, individual residues were demonstrated at 2 ng L^{-1}. As with other components, it is important to determine residue contribution from commonly used consumables.

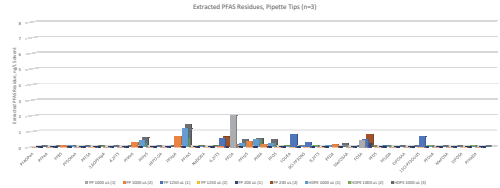

Figure 7. *Pipette Residues, ng L^{-1} extracted.*

EPA 533 Section 8 stipulates the requirement to wear nitrile gloves as a precaution against contamination during sampling. We determined PFAS residue extractable from commercially available nitrile gloves, used in our Cardiff laboratory.

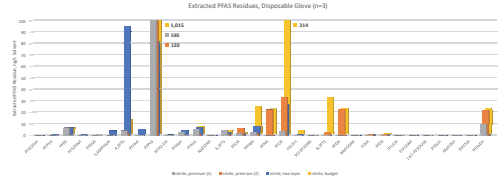

Figure 8. *Disposable Residues, ng L^{-1} extracted.*

Figure 8 demonstrates single use nitrile gloves have extremely high residues. Where present, individual residues are typically between 2 and 40 ng L^{-1}. Three of the 32 measured residues demonstrate concentrations between 80 and 1,000 ng L^{-1} (1 ppb), extreme values were extrapolated and are for indication only. These residues are likely derived from a complex manufacturing process incorporating plasticizers and mold-release compounds. We were not able to demonstrate transfer from glove to test article. However, we believe this level of residue is a cause for concern and should be adequately controlled in the analytical laboratory. Agitation in PFAS free water may reduce glove residues, work is underway to determine possible recommendations.

Conclusion

- We demonstrate commonly observed PFAS residues for 22 of our 32 target analytes.
- 15 of the commonly observed component residues demonstrate elevated PFAS concentrations. Of the 15 target analytes with elevated concentrations, 12 of these were common to one or more class of component tested.
- We demonstrate consumable components of concern that may contribute to laboratory background and be potential causes of false positives.

References

1. Glüge J. et al (2020), An overview of the uses of per- and polyfluoroalkyl substances (PFAS). Environ. Sci.: Processes Impacts, 22: 2345
2. EPA METHOD 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry

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