Comparative Evaluation of Analytical Techniques for PFAS Quantification

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[Introduction]

Per- and polyfluoroalkyl substances (PFAS) are a group of synthetic chemicals extensively used across various industries due to their unique physicochemical properties. The resulting health and environmental impacts of their widespread application have been well documented [1,2]. Despite growing regulatory efforts, accurately detecting and quantifying PFAS remains challenging due to their diverse chemical structures, typically low environmental concentrations, and the complexity of environmental matrices. Moreover, current standardized analytical methods do not provide a comprehensive assessment of total PFAS or total organofluorine content in contaminated samples. Differences in the underlying chemistry of measurement techniques often yield varying estimates for the same sample [3]. This study aims to address these limitations by applying multiple analytical methods to investigate PFAS composition in aqueous film-forming foam (AFFF), with the objective of comparing their effectiveness and limitations in detecting and quantifying PFAS.

[Methods]

Three AFFF samples (AFFF-1, AFFF-2, and AFFF-3) were prepared and analyzed in triplicate using the following protocols: Modified US EPA Method 537.1 (US EPA Method 537.1 M) [4], US EPA Method 1633 [5], MoE Notification (PFAS analysis Method by the Japanese Ministry of the Environment Notification Appendix 1) [6] and our in-house Total Oxidizable Precursor (TOP) assay method [7].

[Results and discussion]

A comparison of the target analytical methods revealed that US EPA Method 1633 has the highest detected total PFAS concentration in the range of 900-25,700 ng/g for all samples, followed by US EPA 537.1 M (960 -14,000 ng/g) and MoE Notification (10-11,140 ng/g) (Figure 1(a)). This trend was expected since US EPA Method 1633 has the capability to test for 40 analytes, and US EPA 537.1 M and MoE Notification can be used to test for the presence of 21 and 4 target PFAS respectively. C4–C8 perfluorocarboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs) were the most frequently detected compounds. PFCA precursors such as 6:2 FTS (detected in AFFF-1 only) and PFOSA (detected in both AFFF-2 and AFFF-3) were identified through the application of US EPA Methods 1633 and US EPA 537.1 M. Post-TOP assay analysis revealed analyte concentrations approximately 2–10 times higher than those obtained via targeted analytical methods, achieving at least 99% oxidation for PFOSA and complete oxidation for other PFCA precursors, except for 6:2 FTS, whose concentration unexpectedly increased in AFFF-1. This increase in 6:2 FTS concentration may be attributed to the presence of 6:2 Fluorotelomer Thioether AmidoSulfonate (trade name: Lodyne), a common AFFF component known to degrade into 6:2 FTS under biological conditions. However, further investigation is needed to determine its behavior during the TOP assay [8]. Moreover, the molar yield of PFOA, a PFOSA post-oxidation product, exceeded 500%, suggesting the presence of undetected precursors contributing to the observed results. US EPA Method 1633 and the MoE Notification method yielded comparable results for PFOA in AFFF-1 (13.8 ± 1.0 ng/g), whereas US EPA 537.1 M reported nearly double the concentration for the same sample. PFOA concentrations for AFFF-2 (1392.0 ± 203.0 ng/g) and AFFF-3 (1513.5 ± 7.9 ng/g) were consistent across all target methods (Figure 1 (b)). The same trend was observed for PFHxS and PFOS in all samples except in AFFF-1 were PFOS could not be detected likely due to matrix interference that suppressed the internal standard signal. These findings suggest that some analytical methods may have difficulty in measuring analytes in complex matrices such as AFFF, due to differences in method reporting limits, quality control criteria, extraction efficiency and/or ion suppression. Pre-treatment steps involving granular activated carbon, as used in Method 1633, can reduce matrix interference and improve analyte detection. Additionally, US EPA Method 1633 detected several PFAS compounds not identified by other methods (e.g., MoE Notification), underscoring the need for method standardization and expanded target analyte lists.

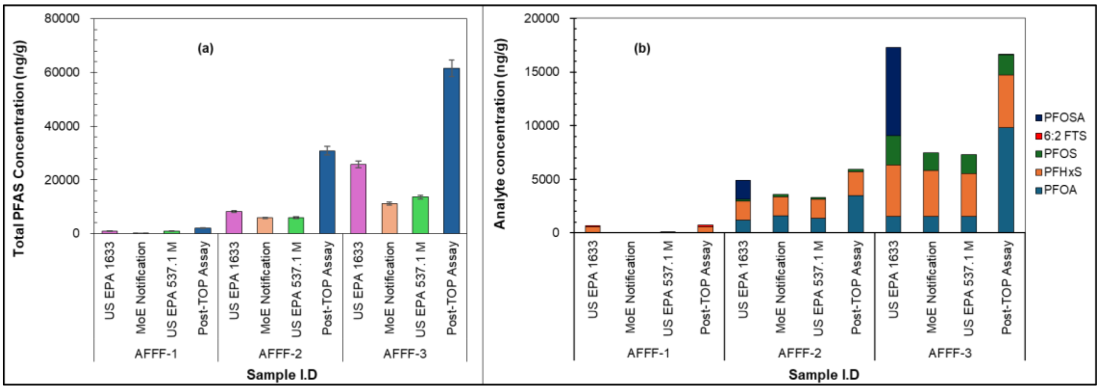

Figure 1: Comparison of PFAS analytical methods (a) Total detected PFAS (b) Results of selected PFAS

[Conclusion]

This study highlights the limitations of currently available analytical methods and emphasizes the need for improved or complementary approaches. The method-specific detection patterns observed reinforce the importance of using multiple analytical techniques to achieve a more comprehensive PFAS profile in complex matrices such as AFFF. Future work will include analysis using our in-house GC-MS method, testing for ultra-short-chain PFAS, ISO 21675, and application of US EPA Method 1621 to determine Adsorbable Organic Fluorine (AOF) concentrations.

[References]

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