

User Guidance: Method for the Determination of Specific Residual Per- and Poly-fluoroalkyl substances (PFAS) in AFFF and AR-AFFF

Method Purpose

- 1) Provides a standardized, validated analytical method to quantitatively determine and report the concentration of specific PFAS substances, aka method analytes (See Table 1), in aqueous film forming foam (AFFF) and alcohol-resistant AFFF (AR-AFFF) concentrates
- 2) Provides a method that reproducibly and reliably achieves limits of quantification for reporting the concentration of method analytes for end-users to comply with regulatory reporting limits. People using data generated by this method should confirm fit of method for any specific PFAS regulation before application.
- 3) Utilizes best principles and practices for identification and quantification, and avoidance of matrix effects to provide accurate and reproducible method analyte concentrations in AFFF and AR-AFFF concentrates.

Applicability

- 1) This method is applicable to the measurement of the specific method analytes shown in Table 1 in AFFF and AR-AFFF concentrates.
- 2) Where mixing with additional water has occurred, please consult with the laboratory to determine sample size characteristics.
- 3) In certain cases, samples may be deliberately diluted for easier handling and sample size selection.
- 4) This method is NOT applicable to fluoroprotein (FP) or film-forming fluoroprotein (FFFP) foams.

Method Analytes and Reporting Limits

- 1) The method is validated for the 29 PFAS method analytes shown in Table 1, including PFOS and PFOA.

- 2) Many of the method analytes are legacy long-chain PFAS that are not expected to be part of AFFF or AR-AFFF foam concentrates under current production that contain only short-chain fluorotelomer-based fluorosurfactants.
- 3) Additional analytes may be added in the future.
- 4) Applicability to FP and FFFP foams may be added in the future.
- 5) Method Reporting Limits – See Table 1.
- 6) Sample pre-screening is recommended at the laboratory to ensure highest concentration analytes are within the method calibration range and that sufficient amounts of surrogate standard are added to allow for isotope dilution quantification.
- 7) When requesting analysis, discuss with the laboratory to ensure clarity on sample amount, collection and shipping procedures.

Sample Bottles and Sampling Media

- 1) AFFF concentrates are typically shipped and stored at ambient temperatures. Laboratories can store these materials cold if necessitated by laboratory quality manual/other processes.
- 2) HDPE containers, with QA control (e.g., method blank) on cleanliness are strongly recommended as part of the method. Only clean HDPE bottles, preferably supplied by the laboratory, are used to send samples for analysis. The laboratory will provide a 250/500 mL wide mouth HDPE container. If laboratory-provided containers are not used, any containers used must be rinsed three times with methanol that is free of PFAS contamination. In this case, an empty bottle rinsed three times with methanol should be provided in addition to the samples for use in the laboratory as a blank. If laboratory provided bottles are not used, contact the laboratory for further information on cleaning/handling of sampling containers.
- 3) It is recommended that at least 100 mL of AFFF concentrate be provided to the laboratory. The amount needed for determination using the method is 0.02 mL. The laboratory will subsample the amount required from the sample provided.
- 4) To ensure that test sample results accurately represent the sample alone, handle samples with caution to provide a representative sample, and to avoid contamination with analytes determined by this Method.
- 5) Preparing the sample to be submitted is very important. Adjacent manufacturing, other products, raw materials and more can contribute significantly to contamination of the sample. Take all precautions to avoid cross-contamination.
 - a. Wear fresh, disposable gloves (nitrile, for example) while handling.
 - b. When transferring samples to the sample bottles, ensure that all surfaces coming into contact with the sample has been cleaned with PFAS-free methanol to avoid contamination of the target analytes.

Safety

All Samples (with the exception of duplicates) must be accompanied by a Safety Data Sheet (SDS) that details hazardous ingredients present, and safe handling, use and disposal procedures. Electronic versions are acceptable. Communication of SDS linked to Sample identification (ID), and other safety information prior to shipping of samples will reduce delays in receiving and analysis.

Shipping and Data Availability

Sample shipping and turnaround times are specific to each laboratory. Typical times range from 20-30 business days from finalization of all details including Sample receipt and contracts.

Study Reports

Reports vary by laboratory but will at the minimum contain concentration and reporting limit for each analyte, quality control criteria for the sample and the batch, any exceptions from method protocols and criteria, and impact of these exceptions. Electronic data deliverables (EDD) may be provided as well.

Potential Limitations

- 1) The method has currently been validated in one laboratory with a select set of AFFF and AR-AFFF concentrate as fit for purpose for the analysis of the target substances (Table 1) in AFFF and AR-AFFF concentrates. Further validation by multiple laboratories and with an expanded set of foam concentrates is part of the next phase of validation.
- 2) Specific sample formulations may pose interferences and other laboratory issues hitherto unobserved. The analytical laboratory shall communicate exceptions from quality control criteria and discuss mitigation options with the client prior to sending final data.
- 3) Analytes present at high levels such as 6:2 FTS, for example, relative to the PFOS/PFOA reporting limit of 10 ng/mL may exceed the method's upper calibration limit and be reported as estimated minimum values. Additional analysis may be required to quantify analytes that are in high concentration relative to others.

Cost

Typical prices per sample for analyses via this method are expected to be between \$300 and \$500 per sample for normal reporting (turnaround) times of 20-30 business days depending on project specifics. Contact the laboratory to finalize contracts and terms prior to sending samples.

Glossary of Terms

- AFFF – Aqueous Film Forming Foam containing fluorinated and hydrocarbon surfactants formulated for class B hydrocarbon fires.
- AR-AFFF – Alcohol-Resistant AFFF containing fluorinated and hydrocarbon surfactants formulated for class B polar solvent and hydrocarbon fires
- Fluoroprotein Foams – Firefighting foams containing fluorinated surfactants and a polymer protein foam base formulated for class B hydrocarbon fires

- Foam Concentrate – Formulation of AFFF/AR-AFFF in concentrate form prior to dilution for deployment
- Method Analytes – List of PFAS that can be reported using this method.
- Sample(s) – Foam concentrate that is to be tested for concentrations of method analytes using this method.

Table 1. Method Analytes

Analyte ¹	Name	Nominal Reporting Limit (ppb or ng/mL)
PFBA	Perfluorobutanoic acid	40
PFPeA	Perfluoropentanoic acid	20
PFHxA	Perfluorohexanoic acid	10
PFHpA	Perfluoroheptanoic acid	10
PFOA	Perfluorooctanoic acid	10
PFNA	Perfluorononanoic acid	10
PFDA	Perfluorodecanoic acid	10
PFUnA	Perfluoroundecanoic acid	10
PFDoA	Perfluorododecanoic acid	10
PFTrDA	Perfluorotridecanoic acid	10
PFTeDA	Perfluorotetradecanoic acid	10
PFBS	Perfluorobutane sulfonic acid	10
PFPeS	Perfluoropentane sulfonic acid	10
PFHxS	Perfluorohexane sulfonic acid	10
PFHpS	Perfluoroheptane sulfonic acid	10
PFOS	Perfluorooctane sulfonic acid	10
PFNS	Perfluorononane sulfonic acid	10
PFDS	Perfluorodecane sulfonic acid	10
PFDoS	Perfluorododecane sulfonic acid	10
4:2 FTS	4:2 fluorotelomer sulfonic acid	40
6:2 FTS	6:2 fluorotelomer sulfonic acid	40

8:2 FTS	8:2 fluorotelomer sulfonic acid	40
PFOSA	Perfluorooctanesulfonamide	10
N-MeFOSA	N-Methylperfluorooctanesulfonamide	10
N-EtFOSA	N-Ethylperfluorooctanesulfonamide	10
N-MeFOSAA	N-Methylperfluorooctanesulfonamidoacetic acid	10
N-EtFOSAA	N-Ethylperfluorooctanesulfonamidoacetic acid	10
N-MeFOSE	N-Methylperfluorooctanesulfonamidoethanol	100
N-EtFOSE	N-Ethylperfluorooctanesulfonamidoethanol	100

¹Target analytes are determined as the total of linear and branched isomers.

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