Guidance for Perfluorochemicals Analysis

The Minnesota Pollution Control Agency (MPCA) has been asked to provide method guidance (along with quality control (QC) acceptance criteria) for the Per- and Polyfluoroalkyl Substances (PFAS) analysis. These criteria should be considered as minimum standards (the laboratory may use stricter criteria) and should be met when analyzing and reporting sample results to the MPCA. The criteria appear below. If there are any questions, please contact the MPCA at 800-657-3864 or 651-296-6300; or see the Quality System webpage located at https://www.pca.state.mn.us/about-mpca/mpca-quality-system.

General considerations

Water and soil/sludge samples are stored at ≤6°C from the time of collection to the time of analysis. Fish tissue is frozen and transported on dry ice.

Sample collection material and sample containers must be demonstrated to be PFAS-free. All preparation and analytical steps must be demonstrated to be PFAS-free. When samples are pre-treated, the laboratory must use the same steps for the associated batch QC samples.

Identification of target analytes is based on retention time windows and a minimum of two fragment ions, if available. The primary transition ion is used for quantification and the secondary transition ion is used for confirmation. The laboratory must ensure that the retention of the target analyte in the sample compares to the retention time of the analyte in the calibration standard and that the primary and secondary fragment ion transitions of the target analyte match those of the analyte in the calibration standard. The laboratory must establish procedures to monitor these ions and note any exceptions to the procedures.

If possible, purchase the target analytes as technical-grade standards or as neat or certified materials. The technical-grade standards contain both the linear and branched isomers. Standards that contain only the linear isomer can be substituted only if technical-grade standards are not available.

The laboratory must clearly define the conditions for acceptable manual integrations in their Quality Assurance Manual. If the laboratory must perform any manual integration, both the original and manually integrated chromatograms are retained with the data package.

Initial Calibration

Either External or Isotope Dilution Standard Calibration techniques can be used. If the External Calibration technique is chosen, see the spiking requirement in the Batch QC Section. If the Isotope Dilution Standard Calibration technique is chosen, 13C-labelled or deuterium-labelled standards are used to correct for recovery of the 33 target analytes. The Isotope Dilution Standards must represent the analyte chemistries of the target analytes. The Isotope Dilution Standards must be added prior to sample preparation. The concentrations of each target analyte is calculated from the average response factor or from the standard curve.

1. Check the instrument operating conditions. Instrument maintenance may be required.
2. Review the response at each calibration level to insure that the problem is not associated with one standard. If the problem appears to be associated with one of the standards, that standard can be re-injected. If the problem persists, re-make the standard and re-analyze it.

3. The last alternative is to delete calibration points from the curve. The MPCA will allow the removal of a calibration point (either the highest level or the lowest level) from the curve under the following provisions. If a non-linear calibration model is used in the initial calibration curve, a quadratic (second order) curve will require at least six non-zero standard levels while a polynomial (third order) curve will require at least seven non-zero standard levels. Care must be taken to insure that there are enough remaining calibration points for the initial calibration curve. If the calibration criteria are now met, the analysis can proceed. However, there are ramifications in removing calibration points. If the top point is removed, the need for diluting samples and re-analyzing will occur at a lower concentration level. If the lowest point in the curve is removed, the sensitivity of the analysis has changed and thus the report level will need to change. This may impact action levels.
4. The Initial Calibration is run initially and as required to maintain calibration verification and sensitivity. Each calibration point in the curve is re-processed using the calibration curve. The calculated concentrations must be within 75% to 125% of the true value (except for the concentration of the lowest calibration point which may be 70% to 130% of the true value). Surrogates recoveries must be within 50% to 200% of the true value.
5. Prior to sample analysis, analyze a second-source standard at a mid-point calibration level. The recoveries must be within 75% to 125% of the true value before analysis can begin.

Continuing Calibration

The Initial Calibration Curves are verified at the beginning and ending of an analytical sequence and every 12 hours by analyzing a mid-level standard. The drift must be within 70% to 130%. If the instrument calibration results are outside the acceptance criteria, check the instrument operating conditions and/or perform instrument maintenance. Re-analyze the calibration standard. If the calibration criteria are still not met, a new Initial Calibration must be performed. All samples that were analyzed since the last passing calibration standard must be re-analyzed. There is one exception allowed for this QC criterion.

If the recovery of the calibration verification standard is >130% of the true value and the environmental samples show no detection of the analyte, the “less than” value can be reported without re-analysis.

Method validation

The laboratory must perform an initial demonstration of low background for each matrix by analyzing instrument blanks and demonstrating that the analytical system is free of contamination and that the method analytes are not detected above one-half the report levels.

The laboratory must also perform an initial demonstration of capability for the analysis of each matrix. Four to seven laboratory control samples near the mid-range of the calibration curve must be prepared and analyzed. The samples must be processed through the entire preparation and analysis procedure. The average percent recovery of the replicate analyses for water samples must be ≥80% and ≤120% (with a relative standard deviation of ≤20%). The average percent recovery for solid matrices must be ≥60% and ≤130% (with a relative standard deviation of ≤50%).

Method detection limits/Report limits

Method detection levels (MDLs) and report levels (RLs) are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. The RLs should be three times the MDLs. The RLs are also the lowest standard in the calibration curves. If the accuracy of the RL standard does not meet the 70% to 130% criteria, new RL standards are chosen and analyzed until the accuracy criteria are met. Contact the MPCA Project Manager for required report levels for each target analyte.

Report levels depend on program needs. They can change as new information becomes available. Report levels are verified after each calibration and at least monthly. For most analytical work for the MPCA, the report levels should be at or below those listed in the following table:

Target Analyte	Acronym	Aqueous Report Levels (ng/L based on 0.5L sample)	Soil/Sludge Report Levels (ng/g based on 5g sample)	Fish Tissue Report Levels (ng/g based on 2g sample)
Perfluorobutanate	PFBA	3.2	0.32	0.8
Perfluoropentanoate	PFPeA	1.6	0.16	0.4
Perfluorohexanoate	PFHxA	0.8	0.08	0.2
Perfluoroheptanoate	PFHpA	0.8	0.08	0.2
Perfluorooctanoate	PFOA	0.8	0.08	0.2
Perfluorononanoate	PFNA	0.8	0.08	0.2
Perfluorodecanoate	PFDA	0.8	0.08	0.2
Perfluoroundecanoate	PFUnA	0.8	0.08	0.2
Perfluorododecanoate	PFDoA	0.8	0.08	0.2
Perfluorotridecanoate	PFTrDA	0.8	0.08	0.2
Perfluorotetradecanoate	PFTeDA	0.8	0.08	0.2
Perfluorobutanesulfonate	PFBS	0.8	0.08	0.2
Perfluoropentanesulfonate	PFPeS	0.8	0.08	0.2
Perfluorohexanesulfonate	PFHxS	0.8	0.08	0.2
Perfluoroheptanesulfonate	PFHpS	0.8	0.08	0.2
Perfluorooctanesulfonate	PFOS	0.8	0.08	0.2
Perfluorononanesulfonate	PFNS	0.8	0.08	0.2
Perfluorodecanesulfonate	PFDS	0.8	0.08	0.2
Perfluorododecanesulfonate	PFDoS	0.8	0.08	0.2
4:2 fluorotelomersulfonate	4:2 FTS	3.2	0.32	0.8
6:2 fluorotelomersulfonate	6:2 FTS	3.2	0.32	0.8
8:2 fluorotelomersulfonate	8:2 FTS	3.2	0.32	0.8
N-Methylperfluorooctanesulfonamidoacetic acid	N-MeFOSAA	0.8	0.08	0.2
N-Methylperfluorooctanesulfonamidoacetic acid	N-EtFOSAA	0.8	0.08	0.2
Perfluorooctanesulfonamide	PFOSA	0.8	0.08	0.2
N-Methylperfluorooctanesulfonamide	N-MeFOSA	0.8	0.08	0.2
N-Ethylperfluorooctanesulfonamide	N-EtFOSA	0.8	0.08	0.2
N-Methylperfluorooctanesulfonamidoethanol	N-MeFOSE	8	0.8	2
N-Ethylperfluorooctanesulfonamidoethanol	N-EtFOSE	8	0.8	2
Perfluoro-2-propoxypropanoate	HFPO-DA	3.2	0.32	0.8
4-dioxa-3H-perfluorononanoate	ADONA	3.2	0.32	0.8
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	3.2	0.32	0.8
11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	3.2	0.32	0.8

Batch QC

A batch is defined as up to 20 environmental samples. At a minimum, each batch must contain a method blank, a Laboratory Control Sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD) pair. If there is not enough sample to prepare and analyze a MS/MSD pair, a Laboratory Control Sample Duplicate (LCSD) is prepared and analyzed. **However, if the External Calibration technique was chosen, every environmental sample must have a matching matrix spike and every sample must be spiked with at least two surrogates to monitor the preparation and analytical steps.**

1. The concentration of each target analyte in the method blank must be less than the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be re-processed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte, which are less than ten times the concentration in the blank, should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte which are above ten times the blank contamination will not need to be qualified.
2. If the External Standard procedure is used, the surrogate recoveries in each sample must be between 50% and 150%.
3. If the Isotope Dilution Standard procedure is used, the individual Isotope Dilution Standard concentrations are calculated using the Initial Calibration curve. The resulting concentrations in each sample must be within 50% to 200% of the true value.
4. All target analytes are to be spiked into the MS or LCS. The spiking levels should be near the mid-point of the calibration curves. The LCS is made from reagent-grade water, clean sand, or fish tissue that has been demonstrated to be PFAS-free. In a water matrix, the percent recoveries of the target analytes in the LCS or MS must be between 70% and 130%. In other matrices, the percent recoveries of the target analytes in the LCS or MS must be between 50% and 150%.
5. The Relative Percent Difference (RPD) between the LCS/LCSD or MS/MSD pairs in water must be less than or equal to 30%. The RPD between the MS/MSD or LCS/LCSD pairs in other matrices must be less than or equal to 50%.
6. If prepared, the RPD between water sample duplicate pairs must be less than or equal to 30%, while in other matrices, the RPD between sample duplicate pairs must be less than or equal to 50%.

Any QC failure that is not remedied by re-analysis or re-extraction/re-analysis must be flagged in the final report and corrective actions detailed (along with an explanation of the impact on data quality) in the case narrative.