DEPARTMENT OF HEALTH

Perfluorinated Chemicals (PFCs) Analytical Checklist

ENVIRONMENTAL LABORATORY ACCREDITATION PROGRAM (MNELAP)

Analytical Documents in Drinking Water, Nonpotable Water, Biological Tissue and Solid and Chemical Material Samples for PFC Compounds by LC/MS/MS

Item #	Item	References	Onsite Observation(s)
Sample Preservation/Sample Storage			
1	Samples are stored at a temperature of 0 - 6°C from the time of collection to the time of analysis. Fish tissue is frozen and transported on dry ice.	MPCA Guidance Document 2009 TNI V1M2 4.4 and 5.8	
2	Sample collection materials or containers are demonstrated as PFC-free (note: PTFE/Teflon and tinfoil potentially transfer PFCs).	MPCA Guidance Document 2009 TNI V1M2 4.4 and 4.6	
Holding Time [from CFR Table unless noted]			
3	N/A		
Sample Size in Field [from CFR Table unless noted]			
4	N/A		
Field Reagent Blanks (FRB)			
5	A field reagent blank must be collected with each sample set. The sample set is composed of samples collected from the same sample site and at the same time. **NOTE: MPCA projects do not require the collection of field blanks.	EPA 537, 8.3.1 Version 1.1	
6	At the laboratory, fill the field blank sample bottle with reagent water and preservatives, seal, and ship to the sampling site along with the sample bottles. For each FRB shipped, an empty sample bottle (no preservatives) must	EPA 537, 8.3.1 Version 1.1	

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	also be shipped. The same batch of preservative must be used for the FRBs as for the field samples. **NOTE: MPCA projects do not require the collection of field blanks.		
7	At the sampling site, the sampler must open the shipped FRB and pour the preserved reagent water into the empty shipped sample bottle, seal and label this bottle as the FRB. The FRB is shipped back to the laboratory along with the samples and analyzed to ensure that PFAAs were not introduced into the sample during sample collection/handling. **NOTE: MPCA projects do not require the collection of field blanks.	EPA 537, 8.3.1 Version 1.1	
8	Analysis of the FRB is required only if a Field Sample contains a method analyte or analytes at or above the MRL. The FRB is processed, extracted and analyzed in exactly the same manner as a Field Sample. **NOTE: MPCA projects do not require the collection of field blanks.	EPA 537, 9.38 Version 1.1	
9	If the method analyte(s) found in the Field Sample is present in the FRB at a concentration greater than 1/3 the MRL, then all samples collected with that FRB are invalid and must be recollected and reanalyzed. **NOTE: MPCA projects do not require the collection of field blanks. If the concentration of the target analyte is more than X10 the concentration in the FRB, the impact on the result is small and the data may be usable.	EPA 537, 9.3.8 Version 1.1	
Sample Size for Preparation			
10	An adequate volume of sample is collected to minimize the effects of contamination attributed to the collection and containment of the sample; to allow sufficient aliquots for a duplicate, spike and matrix spike duplicate of the sample; and to allow sufficient volume for any pre-concentration steps.	2009 TNI V1M2 5.7 2009 TNI V1M2 5.8	
Sample Preparation			
11	Preparation used by the laboratory (e.g. centrifuge, extractions, and filtration) is free of PFC contamination.	MPCA Guidance Document	

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		2009 TNI V1M2 4.4 and 4.6	
12	When samples are pre-treated, the laboratory also uses the same pre-treatment steps for the associated quality control samples.	MPCA Guidance Document 2009 TNI V1M2 4.4	
13	When used, isotopically labeled standards and/or surrogates are added to samples at the time of preparation.	2009 TNI V1M2 4.4	
Method Validation – Initial Demonstration of Capability			
14	**Initial Demonstration of Low System Background** is performed by analyzing instrument blanks and demonstrating that the analytical system is free of contamination and method analytes are not detected above one-half of the RL value for each matrix.	MPCA Guidance Document 2009 TNI V1M2 4.4	
15	Initial Demonstration of Precision is performed by carrying out four (4) to seven (7) laboratory control samples (LCS) near the mid-range of the calibration curve through the entire preparation and analysis procedure and demonstrating that the relative standard deviation of the replicate analyses is <20%. The laboratory must perform an initial demonstration of capability for the analysis of each matrix.	MPCA Guidance Document 2009 TNI V1M2 4.4	
16	Initial Demonstration of Accuracy is performed by carrying the same four (4) to seven (7) laboratory control samples (LCS) as described above and demonstrating that the average recovery of the replicate analyses is within 80-120%. The average percent recovery for solid matrices must be ≥60 percent and ≤130 percent (with a relative standard deviation of ≤50 percent).	MPCA Guidance Document 2009 TNI V1M2 4.4	
Method Detection Limits (MDLs)			
17	MDLs are determined annually	MPCA Guidance Document 2009 TNI V1M2 4.4	

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18	MDLs are determined after a major change to the instrument conditions	MPCA Guidance Document NELAC 5.4.4	
19	MDLs are determined using the procedure described in 40 CFR Part 136, Appendix B	40 CFR Part 136, Appendix B	
Reporting Limits (RLs)			
20	Reporting limits are determined annually	MPCA Guidance Document 2009 TNI V1M2 4.4	
21	Reporting limits are determined after a major change to the instrument conditions	MPCA Guidance Document 2009 TNI V1M2 4.4	
22	The reporting limits should be at least three (3) times the MDL	MPCA Guidance Document 2009 TNI V1M2 4.4	
23	Reporting limits must meet project-specific requirements (see MPCA's Guidance for typical Analyte/matrix report levels). Report levels depend on program needs, please contact the MPCA Project Manager for project specific analyte levels.	MPCA Guidance Document 2009 TNI V1M2 4.4	
24	Reporting limits are at or above the concentration of the lowest standard in the calibration curve	MPCA Guidance Document 2009 TNI V1M2 4.4	
25	Reporting limits are verified after each calibration and at least monthly	MPCA Guidance Document 2009 TNI V1M2 4.4	
26	The reporting limit verification standard (or re-processed calibration standard) recovers within ±30% of the true value	MPCA Guidance Document 2009 TNI V1M2 4.4	
27	If the reporting limit verification standard does not meet the acceptance criteria, the laboratory may elevate the reporting limit to the next calibration standard, if the concentration of the calibration	MPCA Guidance Document	

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	standard meets the RL accuracy criteria upon re-processing.	2009 TNI V1M2 4.4	
Equipment and Equipment Maintenance			
28	Collision gas: meets or exceed instrument manufacturer's specifications	EPA 537 Version 1.1	
29	Desolvation gas: meets or exceed instrument manufacturer's specifications	EPA 537 Version 1.1	
30	HPLC: with binary pump, vacuum degasser, auto sampler, HPLC column and column compartment, and control module	EPA 537 Version 1.1	
31	Tandem Mass Spectrometer: operating parameters are sufficient to meet QC requirements	EPA 537 Version 1.1	
32	Data system capable of meeting requirements for collecting, processing and adequately storing data from the HPLC system	EPA 537 Version 1.1	
Reagents and Standards, Expiration Check			
33	Mobile phases are high purity, PFC-free, and are not stored in fluoropolymer containers.	EPA 537 Version 1.1	
34	Buffers may be used to enhance and stabilize the formation of ions. (e.g. formic acid, ammonium acetate)	EPA 537 Version 1.1	
35	Where possible, traceability shall be to national or international standards of measurement or reference materials.	2009 TNI V1M2 5.6	
36	The laboratory retains the vendor certificate and sample spectra for all standards.	2009 TNI V1M2 4.13	
37	The purity of the standards is evaluated upon receipt. When a compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.	2009 TNI V1M2 5.6 EPA 537, section 7.2 Version 1.	
38	When standards are prepared from neat compounds, the final concentration of primary standard solutions is adjusted for the purity that is listed on the neat compound's label if less than 96% pure.	2009 TNI V1M2 5.6	
39	When pre-prepared standards are used, the laboratory uses the reported value from the vendor and corrects for salt, if not already included in vendor's reported value. Only correct for purity below 96%.	2009 TNI V1M2 5.6	

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40	A secondary source of standard solutions, if available, is used to check calibration standard integrity. If an external second source is unavailable, then a different lot of the standard solution is prepared to check the calibration standard integrity.	2009 TNI V1M2 5.9 2009 TNI V1M4 1.7	
41	Storage conditions for standard solutions are adequate to prevent degradation and contamination. (Note: PFAA Standards, extracts and samples should not come in contact with glass containers or pipettes as these analytes can potentially adsorb to glass surfaces)	EPA 537, rev 1.1, section 4.1 2009 TNI V1M2 5.6	
42	If high purity labeled internal standards, free of the native isomers, are not available, the native isomers must be less than 5% of the reporting level at normal IS spiking concentrations. This item applies only to Internal Standard Calibration.	2009 TNI V1M2 5.6 2009 TNI V1M2 5.9	
Pre-analysis Requirements			
43	The laboratory has a written procedure for verifying system stability prior to analysis (e.g. analysis of a series of blanks and LCS samples)	2009 TNI V1M2 5.9	
Initial Calibration Requirements and Linear Range			
44	**External Standard Calibration:** External standard calibration is allowed. Please see required spiking criteria in QC accuracy.	MPCA Guidance Document 2009 TNI V1M2 4.4	
45	**Internal Standard Calibration (Isotope Dilution Standards or Internal Standards):** Internal Standards must be isotopically labeled compounds representing the target analyte chemistries. Standards must be added prior to sample preparation. A minimum of 4 internal standards are required for the 13 analyte MPCA PFC panel. The internal standards chosen must represent all target analyte chemistries (e.g. acids and sulfonates).	MPCA Guidance Document 2009 TNI V1M2 4.4	
46	Internal Standard Calibration: The individual Internal Standard (or Isotope Dilution Standards) responses in each sample must be within 50 percent to 200 percent of the average individual Internal Standard responses measured during the Initial Calibration.	MPCA Guidance Document 2009 TNI V1M2 4.4	

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47	**Internal Standard Calibration:** Peak area counts for all ISs in all injections must be within ± 50% of the average peak area calculated during the initial calibration. If Internal Standards do not meet this criterion, corresponding target results are invalid.	EPA 537, section 9.3.4 Version 1.1	
48	**Internal Standard Calibration:** Peak area counts for all ISs in all injections must be within 70-140% from the most recent CCC. If Internal Standards do not meet this criterion, corresponding target results are invalid.	EPA 537, section 9.3.4 Version 1.1	
49	**Internal and External Calibrations:** Samples that have concentrations exceeding the highest calibration standard from the ICAL are diluted into the calibration range and reanalyzed	MPCA Guidance Document 2009 TNI V1M2 4.4	
50	The percent relative standard deviation for average response factors must be less than or equal to 20 percent for each analyte.	MPCA Guidance Document 2009 TNI V1M2 4.4	
51	The r^2 value for each analyte curve is ≥ 0.990	MPCA Guidance Document 2009 TNI V1M2 4.4	
52	The recovery for all points in the curve (except the lowest point) is 75-125% of the true value. Lowest point recovery: 70% – 130%	MPCA Guidance Document 2009 TNI V1M2 4.4	
53	When points are removed from a calibration curve that do not meet the acceptance criteria in order to make the curve acceptable, sufficient numbers of points remain if the calibration curve is non- linear. [NOTE: must have 6 non-zero points for linear and quadratic and must have 7 non-zero points for polynomial.]	MPCA Guidance Document 2009 TNI V1M2 4.4	
Calibration Verification Requirements			

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54	A batch may be up to 20 field samples. An analytical sequence may include several batches. The initial calibration curves are verified at the beginning and ending of an analytical sequence for all analytes of interest and every 12 hours by analyzing a mid-level standard.	MPCA Guidance Document 2009 TNI V1M2 4.4	
55	The calculated amount of the mid-level calibration verification standard is within 70% - 130% of the true value.	MPCA Guidance Document 2009 TNI V1M2 4.4	
56	If the criteria are not met, the laboratory performs instrument maintenance and reanalyzes the calibration verification standard after the instrument is stabilized.	MPCA Guidance Document 2009 TNI V1M2 4.4	
57	If after performing instrument maintenance and re-analyzing the calibration verification standard, the criteria still cannot be met, a new ICAL is performed.	MPCA Guidance Document 2009 TNI V1M2 4.4	
58	All samples that were analyzed between a passing calibration verification standard and a failing calibration verification standard are reanalyzed.	MPCA Guidance Document 2009 TNI V1M2 4.4	
59	If a calibration verification standard is >130% of the true value and field samples show no detection of analyte(s) then the less than values may be reported without reanalysis.	MPCA Guidance Document 2009 TNI V1M2 4.4	
Procedure			
60	Samples are analyzed using the same instrument settings and sample injection volume as the calibration standards, method blanks, and quality control determinations.	2009 TNI V1M2 5.9	
61	Identification of compounds are based on HPLC retention time and a minimum of two fragment ion transitions, if available. The primary ion transition is used for quantification; the secondary ion transition is used for confirmation. The method must address at	MPCA Guidance Document 2009 TNI V1M2 4.4	

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	what levels the secondary transition may or may not be observed. *[NOTE: PFBA and PFPeA do not exhibit secondary ion transitions].*		
62	The laboratory must establish retention time windows and ensure that the retention of the target compound in the sample is comparable to the retention time of the target compound in the calibration standard.	2009 TNI V1M2 4.4 2009 TNI V1M4 1.5.4	
63	Primary and secondary fragment ion transitions of the target analytes in the sample match those of the calibration standards.	2009 TNI V1M4 1.5.4	
64	The laboratory has a procedure for monitoring ion suppression/enhancement.	2009 TNI V1M2 5.4.3	
65	If possible, purchase the target analytes as technical-grade standards or neat 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.	MPCA Guidance Document 2009 TNI V1M2 4.4	
66	The primary transition ion is used for quantification and the secondary transition ion is used for confirmation.	MPCA Guidance Document 2009 TNI V1M2 4.4	
Quality Control: Accuracy			
67	One laboratory control sample (LCS) containing all target analytes is analyzed for every batch of up to 20 prepared samples.	MPCA Guidance Document 2009 TNI V1M2 4.4	
68	The LCS concentration is in the range of five (5) to ten (10) times the RLs.	MPCA Guidance Document 2009 TNI V1M2 4.4	
69	The LCS is made from reagent-grade water, clean sand, or fish tissue that has been demonstrated to be PFC-free.	MPCA Guidance Document	
70	The recoveries of the target analytes in the aqueous LCS are between 80% and 120%. In other matrices, the percent recoveries of the target analytes must be between 60 percent and 130 percent.	MPCA Guidance Document 2009 TNI V1M2 4.4	

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71	**External Standard Calibration:** If utilizing the external standard technique 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.	MPCA Guidance Document 2009 TNI V1M2 4.4	
72	One aqueous sample per batch of up to 20 samples must have a matrix/matrix spike duplicate that is fortified with all target analytes (MS/MSD). If there is not enough sample an LCS/LCSD is prepared and analyzed.	MPCA Guidance Document 2009 TNI V1M2 4.4	
73	A minimum of two surrogates must be added to each aqueous sample prior to sample preparation. Surrogates must represent the target analyte chemistries and preferably be isotopically labeled target analytes (e.g. acids, sulfonates). Surrogate recoveries must be between 50% and 150%.	MPCA Guidance Document 2009 TNI V1M2 4.4	
74	**Internal Standard Calibration:** If utilizing the internal standard (or Isotope Dilution Standards) technique, one aqueous sample per batch of up to 20 samples must have a matching matrix spike/matrix spike duplicate that is fortified with all target analytes (MS/MSD). If there is not enough sample, an LCS/LCSD is prepared and analyzed.	MPCA Guidance Document 2009 TNI V1M2 4.4	
75	The recoveries of the target analytes in the MS are between 70% and 130%. In other matrices, the percent recoveries of the target analytes must be between 50 percent and 150 percent.	MPCA Guidance Document 2009 TNI V1M2 4.4	
76	Samples that fail the MS recovery may be reanalyzed, and/or diluted and reanalyzed. If recovery still fails the respective source sample must be flagged.	MPCA Guidance Document 2009 TNI V1M2 4.4	
Quality Control: Precision			
77	One matrix spike/matrix spike duplicate pair is analyzed for every batch of up to 20 environmental samples. If there is not enough sample to prepare and analyze a MS/MSD pair, a Laboratory Control Sample Duplicate (LCSD) is prepared and analyzed.	MPCA Guidance Document 2009 TNI V1M2 4.4	
78	The spiking levels (MS/MSD or LCS/LCSD) should be five (5) to ten (10) times the report levels.	MPCA Guidance Document 2009 TNI V1M2 4.4	

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79	The relative percent difference between a matrix spike duplicate pair (MS/MSD pair) is ≤ 30%. The RPD between the MS/MSD or LCS/LCSD pairs in other matrices must be less than or equal to 50 percent.	MPCA Guidance Document 2009 TNI V1M2 4.4	
80	If prepared, the relative percent difference between water sample duplicates laboratory control duplicate pairs (LCS/LCSD pairs) is ≤ 20%. If prepared in other matrices, the relative percent difference between sample duplicate pairs is ≤ 30%.	MPCA Guidance Document 2009 TNI V1M2 4.4	
Quality Control: Blanks			
81	One method blank is analyzed for every prepared batch of up to 20 environmental samples.	MPCA Guidance Document 2009 TNI V1M2 4.4	
82	The laboratory must monitor area counts for method blank data to establish expected background levels.	2009 TNI V1M4 1.7.4	
83	The concentration of every target analyte in the method blank is less than the reporting limit.	MPCA Guidance Document 2009 TNI V1M2 4.4	
84	A "B" qualifier is assigned to any sample's affected target analyte in which the concentration is less than ten times the concentration in the method blank.	MPCA Guidance Document 2009 TNI V1M2 4.4	
85	A qualifier means that the sample results may contain a bias related to method blank contamination.	MPCA Guidance Document 2009 TNI V1M2 4.4	
86	Samples with concentrations above ten times the method blank contamination are not qualified.	MPCA Guidance Document 2009 TNI V1M2 4.4	
Other Specific Criteria			

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	N/A		
Calculations			
87	The concentration of target analytes is calculated from the standard curve or average response factors.	MPCA Guidance Document 2009 TNI V1M2 5.5	
Report to Client			
88	If actions are taken to meet the QC acceptance criteria (such as re-analysis, re-extraction and re-analysis, dilution of sample matrix, or instrument maintenance), the case narrative report indicates the nature of the action and any impact on quality, if applicable.	MPCA Guidance Document 2009 TNI V1M2 5.10	
Laboratory Documentation			
89	Manual integrations, when performed, must be documented and conditions for acceptable integration must be clearly defined in the laboratory's quality assurance manual.	MPCA Guidance Document 2009 TNI V1M2 4.4	
90	Both the original and manually integrated chromatograms are retained with the data.	MPCA Guidance Document 2009 TNI V1M2 4.4	

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