AOAC SMPR® 2025.001

Standard Method Performance Requirements (SMPRs®) for Per- and Polyfluoroalkyl Substances (PFAS) in Food Packaging Materials

Intended Use: Compliance (ref. 1) Monitoring by Trained Technicians

Purpose

What: AOAC *Standard Method Performance Requirements* (SMPRs®) are voluntary consensus standards developed in accordance with the AOAC policy, "AOAC Due Process for Development of AOAC Non-Method Consensus Standards and Documents." SMPRs describe a scientific community's recommended minimum method performance characteristics and analytical requirements for a specific method-related intended use.

Who: Drafted by AOAC working groups, SMPRs are adopted by AOAC by a consensus of stakeholders affiliated with its integrated science programs and projects which are composed of volunteer subject matter experts representing academia, government, industry, and nonprofit sectors from around the world.

Use: AOAC SMPRs are used in the AOAC core science programs as a resource for AOAC method experts, including expert review panels, in the evaluation of validation study data for methods submitted to the AOAC *Official Methods of Analysis*℠ and AOAC *Performance Tested Methods*℠ programs. AOAC SMPRs also may be used to provide acceptance criteria for the verification of methods and serve as a resource to guide method development and optimization.

1 Applicability

Quantitative analysis of each selected relevant and/or common PFAS (*see* Tables 1 and 2) in food packaging matrices (*see* Tables 3 and 4 for list of target matrices and their characteristics, respectively). Preference will be given to methods that individually quantify all target analytes listed in Table 1 from all respective matrices listed in Table 3 and from as many of the additional PFAS analytes listed in Table 2 as possible.

2 Analytical Technique

Mass spectrometry-based methods are preferred. Methods with parallel analyses (i.e., GC-MS and LC-MS) of single analytical subsample will be accepted provided metrological continuity of the subsample is ensured in the combined method. The SMPR is not intended for reactive, oxidative, hydrolytic, or precursor-based methods.

3 Definitions

Limit of quantitation (LOQ).—Minimum concentration or mass of analyte in a given matrix that can be reported as a quantitative result.

Matrix blank.—Sample containing no more than 30% of the target LOQ for each analyte that is brought through the entire measurement procedure and analyzed in the same manner as a test sample.

Procedural blank.—Sample that does not contain the matrix that is brought through the entire measurement procedure and analyzed in the same manner as a test sample.

Repeatability.—Variation arising when all efforts are made to keep conditions constant by using the same instrument and operator (in the same laboratory) and repeated in the same day. Expressed as the repeatability standard deviation (SD_r); or % repeatability relative standard deviation ($\%RSD_r$).

Reproducibility.—Variation arising when identical test materials are analyzed in different laboratories by different operators on different instruments. Standard deviation or relative standard deviation calculated from among-laboratory data. Expressed as the reproducibility standard deviation (SD_R); or % reproducibility relative standard deviation ($\%RSD_R$).

Total % recovery.—Ratio of calculated concentration versus expected concentration, expressed as a percentage.

4 Method Performance Requirements

See Tables 5–8.

5 System Suitability Tests and/or Analytical Quality Control

Suitable methods will include routine procedural blank analyses and at least one reference material (or if unavailable, matrix spike sample) prior to or concurrent with unknown samples. Measures should be taken to reduce background contamination during each stage of sampling and analysis. Method materials used should be free of analytes and, if possible, contact with fluoropolymer materials should be avoided. Procedural blank concentrations should be ≤LOQ in each batch. In the case of unavoidable background contamination >30% LOQ from sampling and analytical equipment/supplies etc., subtraction of procedural blank concentrations (not signals) from samples may be performed provided procedural blanks used for subtraction are clearly matched to subtracted analyses in time, materials, and analytical batch. If procedural blank subtraction is to be used, method authors should specify procedural blanks be run in triplicate within at least one day or batch, and should be run on at least three different days or batches. For PFAS analytes with only one specific identifying line/wavelength/ion/transition (e.g., LC-MS/MS transition for PFBA and PFPeA), a second confirmation of identity (e.g., high-resolution mass spectrometry, etc.) is needed if reporting results from the analysis (including for method validations).

A branched PFOS standard should be included in the analysis for retention time/signal confirmation of isomers. If method authors intend to report ∑PFOS, then exact PFOS isomer standards used for ∑PFOS analysis and the mechanism of isomer quantification should be specified.

Stability of methacrylate and primary amine analytes should be ensured with stabilizers and/or method stability tests.

6 Reference Material(s)

Reference materials (RMs) may be in production, and interested parties should check the following institutions to keep up to date on any newly available RMs:

Fapas® QC sample FCCS8-PMM26QC: https://fapas.com

U.S. National Institutes of Standards and Technology: https://shop.nist.gov

Deutsches Referenzbüro für Ringversuche und Referenzmaterialien (DRRR), potentially PT samples (article No.) 2011124, 2011265, and 2011259: https://odin.drrr.de/

Code d'Indexation des Matéiaux de Référence (COMAR): https://www.comar.bam.de

Table 1. Target analytes

No.[a]	Common name	Acronym	Alternate acronym	CAS No.	Pubchem CID No.
1	Bis[2-(perfluorohexyl)ethyl] phosphate	6:2 diPAP	6:2/6:2 diPAP	57677-95-9	14550408
2	Bis[2-(perfluorooctyl)ethyl] phosphate	8:2 diPAP	8:2/8:2 diPAP	678-41-1	3022253
3	Bis[2-(perfluorodecyl)ethyl] phosphate	10:2 diPAP	10:2/10:2 diPAP	1895-26-7	3022255
4	[2-(Perfluorooctyl)ethyl], [2-(perfluorohexyl)ethyl] phosphate	6:2/8:2 diPAP	6:2/8:2 diPAP	943913-15-3	101536705
5	2-(Perfluorohexyl)ethane-1-sulfonic acid	6:2 FTS	6:2 FTSA	27619-97-2	119688
6	2-(Perfluorooctyl)ethane-1-sulfonic acid	8:2 FTS	8:2 FTSA	39108-34-4	3016044
7	2-(Perfluorodecyl)ethane-1-sulfonic acid	10:2 FTS	10:2 FTSA	120226-60-0	23136180
8	2-(Perfluorohexyl)ethyl methacrylate	6:2 FTMAc	6:2 FTMAcry	2144-53-8	75066
9	2-(Perfluorohexyl)ethenoic acid	6:2 FTUCA	FHUEA	70887-88-6	85976247
10	2-(Perfluorodecyl)ethenoic acid	10:2 FTUCA	FDUEA	70887-94-4	138396354
11	2-(Perfluorooctyl)ethanoic acid	8:2 FTCA	FOEA	27854-31-5	10994425
12	2-(Perfluorodecyl)ethanoic acid	10:2 FTCA	FDEA	53826-13-4	11028244
13	3-(Perfluoropropyl)propanoic acid	3:3FTCA	FPrPA	356-02-5	2774909
14	3-(Perfluoropentyl)propanoic acid	5:3 FTCA	FPePA	914637-49-3	14632790
15	3-(Perfluoroheptyl)propanoic acid	7:3 FTCA	FHpPA	812-70-4	2783376
16	2-(Perfluorohexyl)ethanol	6:2 FTOH		647-42-7	69537
17	2-(Perfluorooctyl)ethanol	8:2 FTOH	FOET	678-39-7	69619
18	2-(Perfluorodecyl)ethanol	10:2 FTOH	FDET	865-86-1	70083
19	Perfluorooctanesulfonamide	PFOSA		754-91-6	69785
20	Perfluorooctane sulfonamidoacetic acid	FOSAA		2806-24-8	10507011
21	Perfluorooctylsulfonylethylglycine	EtFOSAA	N-EtFOSAA	2991-50-6	18134
22	2-(Perfluorooctyl)ethyl dihydrogen phosphate	8:2 mPAP	8:2 monoPAP	57678-03-2	10143739
23	Bis(2-perfluorooctylsulfonyl-N-ethylaminoethyl) phosphate	diSAmPAP	8:2-diSAmPAP	2965-52-8	102352
24	2-(Perfluorohexyl)ethyl acrylate	6:2 FTAcr	6:2 FTAcry	17527-29-6	87149
25	2-(Perfluorohexyl)ethanoic acid	6:2 FTCA	FHEA	53826-12-3	11783764
26	Perfluorobutylethylsulphonic acid	4:2 FTS	4:2 FTSA	757124-72-4	20734543
27	Perfluorobutanesulfonic acid	PFBS		375-73-5	67815
28	Perfluoropentanesulfonic acid	PFPeS		2706-91-4	75922
29	Perfluorohexanesulfonic acid	PFHxS		355-46-4	67734
30	Perfluoroheptanesulfonic acid	PFHpS		375-92-8	67820
31	Perfluorooctanesulfonic acid	PFOS		1763-23-1	74483
32	Perfluorononanesulfonic acid	PFNS	PFNSA	68259-12-1	86998
33	Perfluorodecane sulfonic acid	PFDS	PFDSA	335-77-3	67636
34	Perfluoroundecanesulfonic acid	PFUnDS	PFUnDSA	749786-16-1	22141518
35	Perfluorododecanesulphonic acid	PFDoDS	PFDoDSA	79780-39-5	3018866
36	Perfluorotridecanesulfonic acid	PFTrDS	PFTrDSA	791563-89-8	21964789
37	Perfluorobutanoic acid	PFBA		375-22-4	9777
38	Perfluoropentanoic acid	PFPeA		2706-90-3	75921
39	Perfluorohexanoic acid	PFHxA		307-24-4	67542
40	Perfluoroheptanoic acid	PFHpA		375-85-9	67818
41	Perfluorooctanoic acid	PFOA		335-67-1	9554
42	Perfluorononanoic acid	PFNA		375-95-1	67821
43	Perfluorodecanoic acid	PFDA		335-76-2	9555
44	Perfluoroundecanoic acid	PFUnDA	PFUDA	2058-94-8	77222

Table 1. (*continued*)

No.[a]	Common name	Acronym	Alternate acronym	CAS No.	Pubchem CID No.
45	Perfluorododecanoic acid	PFDoDA		307-55-1	67545
46	Perfluorotridecanoic acid	PFTrDA		72629-94-8	3018355
47	Perfluorotetradecanoic acid	PFTeDA		376-06-7	67822
48	Perfluorohexadecanoic acid	PFHxDA		67905-19-5	106027
49	Perfluoro(2-methyl-3-oxahexanoic) acid	HFPO-DA	bC6O1 PFECA	13252-13-6	114481
50	4,8-Dioxa-3H-perfluorononanoic acid	ADONA	lC7O2 PFECA	919005-14-4	52915299
51	Perfluoro-11-chloro,octyloxyethanesulfonic acid	8:2 Cl-PFESA	11Cl-PF3OUdS	763051-92-9	15099039
52	Perfluoro-9-chloro,hexyloxyethanesulfonic acid	6:2 Cl-PFESA	9Cl-PF3ONS	756426-58-1	22568738

[a] Analytes 1–20 (highlighted) requires validation at a specific concentration in fiber matrices (*see* Table 7).

7 Validation Guidance

Validation of method recovery and repeatability (reproducibility in multi-laboratory validation) must be conducted at each analyte's target LOQ (point #1; *see* Table 7) and at least two (points #2 and #3; *see* Table 7) additional concentrations, 2–20 times the target LOQ (point #2; Table 7) and 40–100 times the target LOQ (point #3; *see* Table 7). For select analytes #1–20 (*see* Table 1) and #53–58 (*see* Table 2) in fiber matrices, the high concentration validation (point #3, Table 7) should be conducted between 500–2500 µg/kg (ppb), regardless of LOQ (*see* Table 7). The sum of LOQs for required analytes must not exceed 250 µg/kg, AND individual analytes' LOQs must not exceed 20 µg/kg (*see* Table 6). In order for the sum of individual analyte LOQs not to exceed 250 µg/kg, many individual analytes' LOQs will likely need to be ≤4 µg/kg. At each method validation concentration, an incurred reference sample near these concentrations or suitable spiked matrix blank should be analyzed at least in triplicate, as well as corresponding matrix blank. Care should be taken (and method authors need to specify steps taken) to ensure homogeneity of matrix spikes/blanks prior to testing method repeatability, reproducibility, and recovery. Method authors must specify sample sizes that are at least as large as those specified in Table 5.

LOQ is the lowest concentration of the analyte in the test material that has been validated with acceptable method performance (recovery and repeatability) by applying the complete analytical method and identification criteria (2). The following positive identification criteria are to be met simultaneously: *(1)* Retention/appearance time of the analyte specific signal (and internal standard if appropriate) should match the average of that analyte's calibrators (in the same analysis sequence) within ±0.5% for gas chromatography or ±1% for other techniques. *(2)* At least one other analyte qualifier/identifying spectral line/wavelength/ion/transition's signal should similarly match calibrators retention times and present a signal-to-noise (S/N) ratio ≥3:1 (the method must include the specific technique used to calculate S/N). *(3)* The

Table 2. Optional analytes to consider

No.[a]	Common name	Acronym	Alternate acronym	CAS No.	Pubchem CID No.
53	(Perfluorodecyl)ethyl (perfluorooctyl)ethyl hydrogen phosphate	8:2/10:2 diPAP		1158182-60-5	138394219
54	Bis(perfluorooctyl-ethylsulfanylmethyl)-dioxaphosphinaneoxide	8:2-FTMAP	8:2/8:2-diFTMAP	NA[b]	15034801
55	Bis(perfluorohexyl-ethylsulfanylmethyl)-dioxaphosphinaneoxide	6:2-FTMAP	6:2/6:2 diFTMAP	NA	156620404
56	Perfluorbutyl-ethanoic acid	4:2 FTCA	FBEA	70887-89-7	15544178
57	Perfluoroheptadecanoic acid	PFHpDA	PFHpDA	57475-95-3	12731199
58	Pentafluoropropionic acid	PFPrA		422-64-0	62356
59	Perfluorooctadecanoic acid	PFODA		16517-11-6	167547
60	Perfluoropentadecanoic acid	PFPeDA	PFPeDA	141074-63-7	12731198
61	Perfluoro-dimethyloctanoic acid	PF-DMOA	PF-3,7-DMOA	172155-07-6	2776093
62	Perfluorooctyl phosphate	6:2 mPAP	6:2 monoPAP	57678-01-0	14250578
63	2-(Perfluorododecyl)ethane-1-sulfonic acid	12:2 FTS	12:2 FTSA	1034143-66-2	23136183
64	2-(Perfluorohexadecyl)ethanol	16:2 FTOH	16:2FTOH	65104-67-8	103202
65	Perfluorobutane sulfonamido acetic acid	FBSAA	FBSAA	347872-22-4	10784527

[a] Analytes 53–58 (highlighted) require validation at a specific concentration in fiber matrices (*see* Table 7).
[b] NA = Not available.

Table 3. Target food packaging matrices

Matrix category	Some typical, representative examples
Paper	Grease-resistant hot sandwich take-away bag, microwave popcorn bag
Paperboard, cardboard	Grease-resistant picnicware plate/bowl, take-away hot entree box, clamshell
Molded fiber	Grease-resistant take-away hot entree clamshell, picnicware plate/bowl
Flexible plastics/blown films	Chocolate bar wrappers, clear cookie sleeves/windows

Table 4. Food packaging matrix characteristics

Matrix	Description	Approximate basis weights, g/m^2
Paper	Flexible, business card thickness or less, semi-translucent under direct light	~12–150
Paperboard	Semi-rigid, thicker than business card, thinner than corrugated cardboard, no visible or structured opposing layers	~150–450
Cardboard	Rigid, structured, visible opposing layers	~220–800
Molded fiber	Rigid/semi-rigid, ~>3 mm thick, no opposing layers, often curved 3-D shapes, one rougher/textured side	~200–1200
Plastic	Flexible/semi-rigid, noncellulosic polymer, molded/extruded/blown	NA[a]

[a] NA = Not applicable.

Table 5. Recommended minimum sample sizes

Sample	Paper	Paperboard/cardboard	Molded fiber	Plastic
Minimum sample size, mg	150	1000	1500	300

Table 6. Maximum target limits of quantification (LOQ) for analytes[a]

Individual analytes' LOQs, µg/kg	Σ Required analyte's LOQs, µg/kg
≤20	≤250

[a] Target concentrations are expressed on w/w basis in samples as received for testing. Values may be revised in the future based on new regulatory requirements.

Table 7. Target method validation concentrations for analytes[a]

Matrix	Point #1	Point #2	Point #3
Paper/board/molded fiber	LOQ	2–20X LOQ	40–100X LOQ[b]
Flexible plastics	LOQ	2–20X LOQ	40–100X LOQ

[a] *See* Section 7 Validation Guidance for additional details.

[b] Method validation point #3 for analytes 1–20 and 53–58 (Tables 1 and 2, respectively) in fiber-based matrix should be conducted between 500–2500 µg/kg (w/w), regardless of LOQ.

Table 8. Acceptable recovery, repeatability, and reproducibility

Parameter	Analytes/points ≥10 µg/kg[a]	Analytes with LOQ <10 µg/kg[a]
Recovery, %	60–115	50–120
Repeatability, RSD_r, %	≤20	≤25
Reproducibility, RSD_R, %	≤30	≤40

[a] For analytes without commercially available matching surrogates/internal standards, recoveries of 40–140% and RSD_r ≤ 30% might be acceptable.

ratios of these other characteristic spectral lines, wavelengths, mass spectral ions or transitions to the quantifying signal shall match the average ratio in standard calibrators in the same analytical batch to within ±30% relative tolerance.

A matrix blank is considered suitable if it contains no more than 30% of the target LOQ level for the given analyte. For method validation, method developers should select at least one representative matrix blank/reference material from each matrix category listed in Table 3. Refer to Table 4 for general food packaging matrix characteristics. Preference will be given to methods applicable to all analyte/matrix combinations listed in Table 3 and as many other Table 2 analyte/matrix category combinations as possible.

If a suitable matrix blank (background or incurred analytes present at <30% of the target LOQ for that analyte) cannot be found for a matrix/analyte, then those PFAS analyte concentrations in that matrix should be determined more precisely with at least seven whole method replicates (including sample handling/subdivision) across days/analysts/consumables. Then spiking experiments for recovery/repeatability should be conducted to achieve concentrations in the evaluated matrix listed in Table 7 (Target Method Validation Concentrations for Analytes). At the conclusion of any spike and recovery study, the previously determined background/incurred PFAS concentration is subtracted from spiked samples for recovery calculations.

Only in the case where there is unavoidable background contamination of an analyte(s) in the matrix blanks that exceeds the target LOQ for those incurred residues, then the LOQ can alternately be calculated for those specific analytes/matrices using the seven "blank" matrix replicates described previously by use of the following equation:

$$LOQ = 10*S_s$$

where S_s is equal to the sample standard deviation of the replicate "matrix blank" samples.

In all other analytes/matrices, LOQ remains defined as the lowest concentration of the analyte in the test material that has been validated with acceptable performance (recovery and repeatability).

Recovery is the fraction or percentage of known/added analyte that is measured or estimated by the method when the reference or spiked sample is analyzed using the entire method. For isotope dilution quantification methods, the estimated target analyte concentration after normalization to the isotopically labeled analog is used to calculate the method recovery.

8 Maximum Time-to-Result

None.

References

(1) Commision Resolution (EU) 2024/TA-9-2024-0318 proposal for a regulation of the European Parliament and of the Council on packaging and packaging waste, amending Regulation (EU) 2019/1020 and Directive (EU) 2019/904, and repealing Directive 94/62/EC [COM(2022)0677–C9-0400/2022–2022/0396(COD)]. EU Parliment Proceedings April 24, 2024. https://www.europarl.europa.eu/doceo/document/TA-9-2024-0318_EN.pdf

(2) EURL for halogenated POPs in feed and food (2022) *Guidance Document on Analytical Parameters for the Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Food and Feed*, version 1.2 of 11 May 2022. https://eurl-pops.eu/core-workinggroups#_pfas

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