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Standard Guide for Determination of Airborne PFAS in the Indoor Air Environment¹

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1. Scope

1.1 This guide describes methods for determining Per- and Polyfluoroalkyl Substances (PFAS) concentrations in indoor air.

1.2 This guide is focused on PFAS measurement technologies applicable to indoor air (including in vehicles and indoor workplaces) and other relevant air volumes such as, air in chambers, bags, or both. The described technologies were developed for indoor air; they may or may not be applicable to other types of air samples.

1.3 This guide describes available technologies and methods that can be used to measure indoor air PFAS concentrations in the gaseous or particulate phases, or both, in indoor air.

1.4 This guide describes each method and its advantages and limitations.

1.5 This guide does not attempt to differentiate between the effectiveness of the methods nor determine equivalence of the methods.

1.6 The sorbent-based sampling strategies addressed in this guide are for PFAS compounds with a molecular mass greater than 200 g mol^{-1} (**1, 2, 3**).² Compounds less than 200 g mol^{-1} , such as CF_4 , C_2F_6 , or PFAS degradation products may require real-time analytical methods described in this guide or other methods that are not presented here.

1.7 *Units*—The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.9 *This international standard was developed in accordance with internationally recognized principles on standard-*

ization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:³

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D6196 Practice for Choosing Sorbents, Sampling Parameters and Thermal Desorption Analytical Conditions for Monitoring Volatile Organic Chemicals in Air

D7968 Test Method for Determination of Polyfluorinated Compounds in Soil by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

D7979 Test Method for Determination of Per- and Polyfluoroalkyl Substances in Water, Sludge, Influent, Effluent, and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

D8141 Guide for Selecting Volatile Organic Compounds (VOCs) and Semi-Volatile Organic Compounds (SVOCs) Emission Testing Methods to Determine Emission Parameters for Modeling of Indoor Environments

D8421 Test Method for Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Matrices by Cosolvation followed by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

D8535 Test Method for Determination of Per- and Polyfluoroalkyl Substances (PFAS) in Soil/Biosolid Matrices by Solvent Extraction, Filtering, and Followed by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)

E3302 Guide for PFAS Analytical Methods Selection

2.2 EPA Standards:⁴

EPA Method 537.1 Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by

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² The boldface numbers in parentheses refer to a list of references at the end of this standard.

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

⁴ Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

Solid Phase Extraction and Liquid Chromatography/
Tandem Mass Spectrometry (LC/MS/MS)

US EPA Method 533 Determination of per- and polyfluoroalkyl substances in drinking water by isotope dilution anion exchange solid phase extraction and liquid chromatography/tandem mass spectrometry

US EPA Method 8327 Per- and Polyfluoroalkyl Substances (PFAS) by Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

US EPA OTM-45 Other Test Method 45 Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources

2.3 ISO Standards:⁵

ISO 16000-6 Indoor air — Part 6: Determination of organic compounds (VVOC, VOC, SVOC) in indoor and test chamber air by active sampling on sorbent tubes, thermal desorption and gas chromatography using MS or MS FID

ISO 16017-1 Indoor, ambient and workplace air — Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography — Part 1: Pumped sampling

3. Terminology

3.1 For definitions of terms commonly used for sampling and analysis of atmospheres, refer to Terminology D1356.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *perfluoroalkyl and polyfluoroalkyl substances (PFAS)*, *n*—fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom.

3.2.1.1 *Discussion*—Perfluoroalkyl chemicals are those chemicals where all hydrogen (H) atoms associated with the carbon (C) atoms of an aliphatic chain have been replaced by fluorine (F) atoms. Polyfluoroalkyl chemicals are those chemicals in which not all H atoms of the aliphatic chain have been replaced by F atoms. Not all PFAS will be found in air (Section 6) and not all PFAS have quantifiable airborne methods (Section 7).

3.2.2 *perfluorooctane sulfonic acid (PFOS)*, *n*—a chemical compound having an eight-carbon fluorocarbon chain and a sulfonic acid functional group.

⁵ Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <https://www.iso.org>.

3.3 Acronyms:

5MS	5 %-Phenyl 95 % methylpoly/arylene siloxane
ACFs	Activated carbon fiber felts
AOF	Adsorbable organic fluorine
CI	Chemical ionization
CIC	Combustion ion chromatography
CIMS	Chemical ionization mass spectrometer
diPAP	Fluorotelomer phosphate diester
DPPO	2,6-diphenyl-p-phenylene oxide
EI	Electron ionization
EOF	Extractable organic fluorine
EtFOSA	N-Ethyl perfluorooctane sulfonamide
EtFOSE	N-Ethyl perfluorooctane sulfonamido ethanol
ESI	Electrospray ionization
FASAs	Fluoroalkyl sulfonamides
FASEs	Fluoroalkyl sulfonamido ethanols
FBET	2-Perfluorobutyl ethanol (4:2)
FDFT	2-Perfluorodecyl ethanol (10:2)
FHEA	2-Perfluorohexyl ethanoic acid (6:2)
FHET	2-Perfluorohexyl ethanol (6:2)
FMACrs	Fluorotelomer methacrylates
FOEA	2-Perfluorooctyl ethanoic acid (8:2)
FOSA	Perfluorooctane sulfonamide
FOSAs	Referring to combination of MeFOSA and EtFOSA
FOET	2-Perfluorooctyl ethanol (8:2)
FTA	Fluorotelomer acids
FTACrs	Fluorotelomer acrylates
FTUCAs	Fluorotelomer unsaturated carboxylic acids
FTOHs	Fluorotelomer alcohols
GC	Gas chromatography
GFFs	Glass fiber filters
HPLC	High-performance liquid chromatography
HFPO-DA	Hexafluoropropylene oxide dimer acid
HRMS	High-resolution mass spectrometry
IDL	Instrument detection limit
LC	Liquid chromatography
MeFBSA	N-Methyl perfluorobutane sulfonamide
MeFBSE	N-Methyl perfluorobutane sulfonamido ethanol
MeFOSA	N-Methyl perfluorooctane sulfonamide
MeFOSE	N-Methyl perfluorooctane sulfonamido ethanol
MeFOSEA	N-Methyl perfluorooctane sulfonamidethyl acrylate
MDL	Method detection limit
MTBE	Methyl tert-butyl ether
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
NCI	Negative chemical ionization
ND	Non-detect
NPSSDBR	Nonionic polystyrene divinylbenzene resin
OECD	Organization for Economic Co-operation and Development
PAHs	Polycyclic aromatic hydrocarbons
PAPs	Polyfluoroalkyl phosphoric acid esters
PCBs	Polychlorinated biphenyls
PCI	Positive chemical ionization
PE	Polyethylene
PEG	Polyethylene glycol
PFAAs	Perfluoroalkyl acids
PFAS	Perfluoroalkyl and Polyfluoroalkyl Substances
PFASA	Perfluoroalkane sulfonamides
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFCAs	Perfluorocarboxylic acids
PFDA	Perfluorodecanoic acid

PFE	Pressurized fluid extraction
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFOSA	Perfluorooctanesulfonamide
PFPeA	Perfluoropentanoic acid
PFPeS	Perfluoropentane sulfonic acid
PFSAs	Perfluoroalkane sulfonic acids
PFTA	Perfluorotetradecanoic acid
PIGE	Particle-induced gamma ray-emission spectroscopy
PLOT	Porous layer open tubular
PM	Particulate matter
PPT	Part per trillion on a molar basis
PTFE	Polytetrafluoroethylene
PTR-MS	Proton transfer reaction mass spectrometry
PUF	Polyurethane foam
QA/QC	Quality assurance and quality control
QFFs	Quartz fiber filters
Q-Trap-MS	Quadrupole-Trap mass spectrometry
RH	Relative humidity
SIFT-MS	Selected-ion flow-tube mass spectrometry
SIM	Selective ion monitoring
SIP	Sorbent-impregnated PUF
SPE	Solid-phase extraction
SVOCs	Semivolatile organic compounds
TD	Thermal desorption
TOF-MS	Time-of-flight mass spectrometry
TOP	Total oxidizable precursor
UHPLC	Ultra-high performance liquid chromatography
UPLC	Ultra performance liquid chromatography
US EPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
VVOCs	Very volatile organic compounds
WCOT	Wall-coated open tubular

4. Summary of Guide

4.1 This guide is intended to provide the user with an overview of (1) the types of PFAS measured in air (Section 6) and (2) the range and applicability of published methods for measuring PFAS in indoor air.

4.2 This guide describes a range of airborne PFAS sampling methods, and the advantages and limitations for each method. These descriptions include both passive and active sampling methods (Section 7), extraction and separation methods (Section 8), and analytical methodologies (for example, gas chromatograph, liquid chromatograph, Section 9).

4.3 This guide discusses published analytical methods that have been used in the analysis of PFAS in air. This guide is not intended to be a comprehensive list of all possible collection and sampling methods for indoor air PFAS.

5. Significance and Use

5.1 Some PFAS have been implicated in adverse human health impacts (4, 5, 6). Therefore, quantifying PFAS concentrations in indoor air is important for accurate and meaningful exposure analysis and risk assessments.

5.2 PFAS found in air can have a wide range of chemical characteristics that will impact sampling practice selection. For example, estimated vapor pressure values can vary by ten orders of magnitude, while estimated Henry's Law constants can vary by five orders of magnitude (Table 1). This means that sampling and analytical methods that are appropriate for one PFAS compound may not be appropriate for other PFAS

compounds. Hence, prior to sampling and selecting analytic methods for PFAS measurement in indoor air, it is critical to establish that the chosen PFAS sampling method(s) is appropriate for the target compound(s), the sampling location, and the environmental conditions.

5.3 The measurement of PFAS in indoor air is an active and growing research topic. Understanding of PFAS properties, sampling and analytic approaches and techniques is constantly evolving. This includes the determination of physical-chemical properties of many PFAS, which may not even have been measured experimentally or which have a wide range of experimentally determined properties (that is, 8:2 FTOH in Table 1). This guide describes methods that are in use at the time of publication.

5.4 PFAS in indoor air may come from a wide range of sources, including consumer products, building materials, food packaging, outdoor air, and other miscellaneous sources. PFAS is also commonly quantified in indoor dust. There are several methods that quantify these chemicals in solid and liquid media including, but not limited to Guide E3302, Test Method D7968, Test Method D7979, Test Method D8421, Test Method D8535, US EPA 533, and US EPA 537.1. US EPA OTM-45 quantifies some PFAS in the combined gas and particle phases of stationary sources, such as incinerator stack sampling.

5.5 This guide is applicable to sampling PFAS in indoor air (typically 15 °C to 30 °C, 20 % to 80 % relative humidity (RH)). While sources like soil vapor intrusion impact indoor air, the methods described here have not necessarily been applied or verified in other gaseous environments, such as soil pore vapor, stack samples, or under ambient outdoor air conditions (<10 °C, >30 °C, <20 % RH, >80 % RH). The methods and information presented here may apply or be compatible with determination of other PFAS or PFAS-like compounds, such as freons and greenhouse gases in other environments, including other collection and acquisition schemes, such as canister methods. However, the scope of this guide is limited to observationally reported PFAS in indoor air.

6. PFAS in Indoor Air

6.1 Both perfluoroalkyl and polyfluoroalkyl substances have been found in indoor air. Perfluoroalkyl chemicals are those chemicals where all hydrogen (H) atoms associated with the carbon (C) atoms of an aliphatic chain have been replaced by fluorine (F) atoms. In contrast, polyfluoroalkyl chemicals are those chemicals in which not all H atoms of the aliphatic chain have been replaced by F atoms (Guide E3302). Either group may contain functional groups with carbon, sulfur, oxygen, or other atoms. Based on the most recent Organization for Economic Co-operation and Development (OECD) definition, PFAS are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom, although a few exceptions exist.

6.2 Thousands of different PFAS have been produced, with a wide range of production volumes. PFAS can be found in air both sorbed onto particles and in the gas phase. Based on their vapor pressures, PFAS sometimes are classified using generic terms like very volatile organic compounds (VVOCs), volatile

TABLE 1 PFAS Previously Identified in Indoor Air and Relevant Chemical Properties

PFAS Group	Representative Compound of Interest	CAS RN	Predicted Henry's Law Constant (HLC or K_H), range, Pa m ³ mol ⁻¹	Experimental HLC or K_H , range, Pa m ³ mol ⁻¹	Predicted Vapor Pressure, range, Pa @ 25 °C	Experimental Vapor Pressure, range, Pa @ 25 °C	References
Fluorotelomer alcohols (FTOHs)	6:2 FTOH	647-42-7	2.65e-5	NA	50.9 to 293	10.0 to 876	(8, 9, 10)
	8:2 FTOH	678-39-7	2.10e-5	NA	22.7 to 30.9	1.64 to 316 000	(8, 9, 10)
	10:2 FTOH	865-86-1	3.72e-5	NA	2.77 to 8.25	8.31e-2 to 79 500	(8, 9, 10)
Fluorotelomer acrylates (FTACr)	8:2 FTACr	27905-45-9	5.25e-1	NA	7.45 to 38.4	NA	(8)
	10:2 FTACr	17741-60-5	1.49e-3	NA	1.27 to 21.2	NA	(8)
Fluorotelomer methacrylates (FTMACr)	6:2 FTMACr	2144-53-8	5.21e-1	NA	5.76 to 57.2	NA	(8)
Fluoroalkyl sulfonamides (FASAs)	N-Methyl perfluorobutane sulfonamide (MeFBSA)	68298-12-4	3.22e-5	NA	3.43 to 549	NA	(8)
	Perfluorooctane sulfonamide (FOSA)	754-91-6	1.28e-4	NA	10.5 to 127	33.1	(8)
	N-Ethyl perfluorooctane sulfonamide (EtFOSA)	4151-50-2	1.62e-5	NA	6.69e-4 to 72.1	5.69e-5 to 7.00	(8, 10, 11)
	N-Methyl perfluorooctane sulfonamide (MeFOSA)	31506-32-8	1.28e-4	NA	1.60e-2 to 112	NA	(8)
	N-Methyl perfluorobutane sulfonamido ethanol (MeFBSE)	34454-97-2	2.67e-5	NA	5.58e-2 to 19.2	NA	(8)
Fluoroalkyl sulfonamido ethanols (FASEs)	N-Ethyl perfluorooctane sulfonamido ethanol (EtFOSE)	1691-99-2	1.52e-5	NA	4.52e-3 to 10.6	1.71e-3 to 0.507	(8, 10)
	N-Methyl perfluorooctane sulfonamido ethanol (MeFOSE)	24448-09-7	1.54e-5	NA	1.35e-3 to 15.6	4.00e-4 to 0.708	(8, 10)
	Perfluorobutanoic acid (PFBA)	375-22-4	5.08	NA	523 to 4480	587 to 98 000	(8, 11)
Perfluoroalkyl carboxylic acids (PFCAs)	Perfluoropentanoic acid (PFPeA)	2706-90-3	3.01e-5	NA	123 to 1060	NA	(8)
	Perfluorohexanoic acid (PFHxA)	307-24-4	2.38e-5	NA	120 to 412	121	(8)
	Perfluorooctanoic acid (PFOA)	335-67-1	1.95e-5	NA	14.8 to 46.0	2.20 to 1330	(8, 12)
	Perfluorononanoic acid (PFNA)	375-95-1	1.20e-4	NA	1.13 to 22.8	0.640 to 1.30	(8, 12)
	Perfluorodecanoic acid (PFDA)	335-76-2	1.52e-5	NA	0.195 to 6.17	0.100 to 0.232	(8, 12)
	Perfluoroalkane sulfonic acids (PFASs)	Perfluorobutane sulfonic acid (PFBS)	375-73-5; 59933-66-3	2.99e-5	NA	1.52e-6 to 27.7	NA
Perfluoropentane sulfonic acid (PFPS)		2706-91-4	2.19e-5	NA	3.76e-5	NA	(8)
Perfluorohexane sulfonic acid (PFHxS)		355-46-4	1.97e-5	NA	1.09e-6	1.08e-6	(8)
Perfluorooctane sulfonic acid (PFOS)		1763-23-1	1.82e-6	NA	3.31e-4	3.31e-4	(8)
Perfluorodecane sulfonic acid (PFDS)		335-77-3	3.35e-5	NA	1.09e-3	NA	(8)
Polyfluoroalkyl phosphoric acid esters (PAPs)	6:2 diPAP	57677-95-9	1.46e-6	NA	7.85e-4 to 4.28e-3	NA	(8)
	8:2 diPAP	678-41-1	1.08e-5	NA	1.79e-5 to 2.48e-5	NA	(8)

organic compounds (VOCs), and semivolatile organic compounds (SVOCs). Guide D8141 demonstrates that criteria defining these classifications can depend on the defining organization. In general, the vapor pressure delineation between a VVOC and a VOC is typically defined as 15 kPa, while the delineation between a VOC and a SVOC is typically at 10^{-8} kPa (Guide D8141). Importantly, characteristics of PFAS in air and their analytical responses do not always correlate to the vapor pressures of the individual chemicals. Table 1 lists eight major groups of PFAS that have been experimentally observed in indoor air. Table 1 lists both estimated and experimentally-determined Henry’s Law constants and vapor pressures for each chemical. Given the relatively recent nature of PFAS research and the large number of different PFAS compounds, most PFAS do not have experimentally-determined chemical properties reported in the literature.

6.3 Within each group, PFAS can have a wide range of chemical properties. For example, perfluorocarboxylic acids (PFCAs) have estimated Henry’s Law constants and vapor pressures that vary by multiple orders of magnitude. This indicates the potential need for chemical-specific and not class- or group-specific measurement strategies of these PFAS in air.

6.4 Fig. 1 and Fig. 2 present how this range of Henry’s Law constants and vapor pressures for PFAS compare to more traditional chemicals quantified in indoor air.

6.5 Table 2 presents the range of PFAS concentrations that have been measured to-date in indoor air for the eight groups of chemicals found in Table 1. Measured PFAS concentrations in air have ranged from non-detect (ND) to 135 000 ng m^{-3} . However, most PFAS have been quantified with indoor air concentrations below 100 ng m^{-3} . Indoor air PFAS concentrations are a function of the indoor conditions, source emissions strength, space volume, space surface, ventilation rate, particle concentration, particle surface pH, and sorption/deposition of the specific chemical.

6.6 Method detection limits (MDLs) depend on the chemical, the instrument, the extraction method (if required) and the analytical method, as well as on background concentrations in field blanks. The ubiquitous presence of PFAS requires appropriate quality assurance and control procedures

(Section 10). MDLs reported in recently published literature are summarized in Appendix X1 (Table X1.1). Most sorbent-based MDLs in these analyses were below 10 pg m^{-3} , with some as low as 0.01 pg m^{-3} . Chemical ionization mass spectrometry (CIMS) MDLs can be orders of magnitude higher than sorbent-based methods due to the sampling durations of seconds rather than hours.

7. Sampling of PFAS in Indoor Air

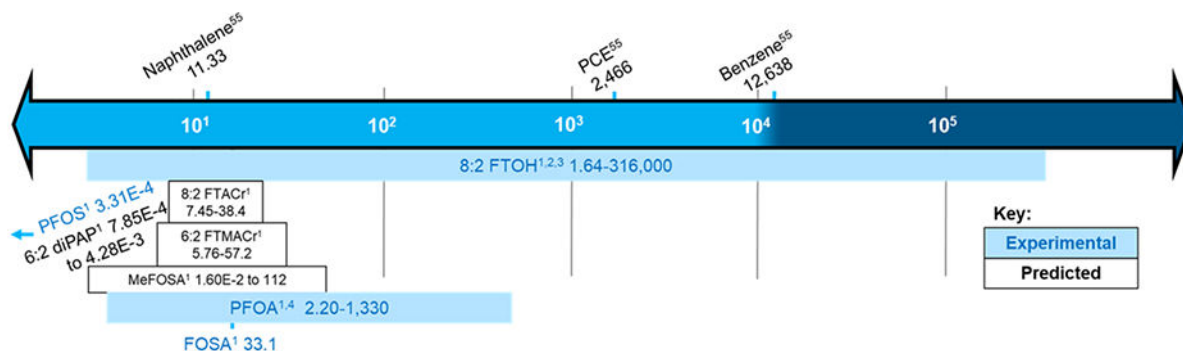
7.1 Identifying and quantifying PFAS in indoor air requires fit-for-purpose sampling. Prior to choosing a sampling method, the intent of the data collection should be established (Guide E3302). Need for airborne PFAS sampling can occur for several reasons that impact the choice of sampling and analysis method.

7.1.1 Indoor air can be sampled for qualitative screening purposes or can be sampled for qualitative and quantitative determination.

7.1.2 Indoor PFAS air sampling in field conditions can impart different requirements for analytical methods than for controlled laboratory sampling conditions.

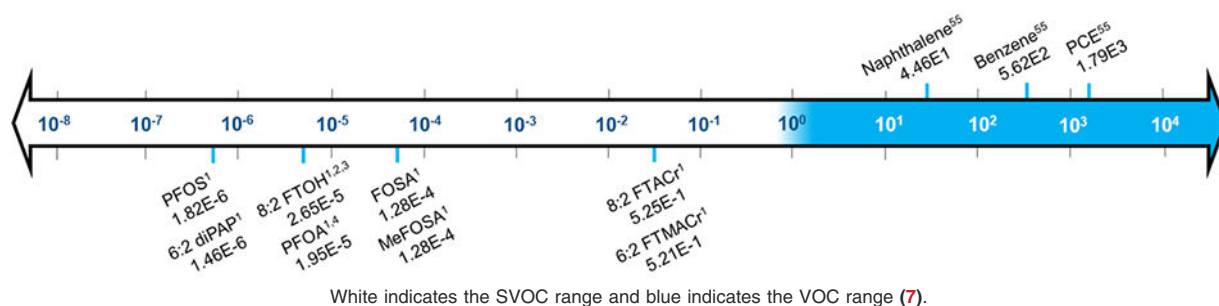
7.1.3 Sampling can take the form of integrative, time-averaged sampling over days or weeks, and can also be performed for shorter time periods of seconds to hours. The analytical technique and required measurement sensitivity influences the minimum and maximum sampling times as a function of the sampler breakthrough for compounds of interest (in sorbent-based techniques) and the overall sensitivity of the technique. However, breakthrough data for many sorbent-based methods and sampling techniques is currently unknown or infrequently reported for most analytes of interest.

7.2 Some PFAS predominantly exist in their speciated, polar form at typical environmental pH levels. This is particularly the case for many perfluoroalkyl acids (PFAAs), for example, perfluorooctanoic acid (PFOA), perfluorooctane sulfonic acid (PFOS), and the polyfluoroalkyl phosphoric acid esters. Hence, they are mostly associated with airborne hygroscopic particles and will only be present in the gas phase at low concentrations, if at all. Uncharged, non-speciated PFAS may also partition to organic components of particles. In contrast, other PFAS such as fluorotelomer alcohols (FTOHs) will be primarily present in the gas phase. Some airborne sampling methods are specific to



Guide D8141 volatility ranges are demonstrated by shading. Dark blue indicates the VVOC range and blue indicates the VOC range.

FIG. 1 Vapor Pressures (Pa at 25 °C) for Select PFAS and Other Typically Analyzed Chemicals in Indoor Air



White indicates the SVOC range and blue indicates the VOC range (7).

FIG. 2 Predicted Henry’s Law Constant (Pa*m³ mol⁻¹ at 25 °C) for Select PFAS and Other Typically Analyzed Chemicals in Indoor Air

TABLE 2 Observational Concentrations of PFAS in Indoor Air

PFAS Group	Representative Compound of Interest	CAS RN	Concentration in Indoor Air (Total Air), range, ng m ⁻³	References
Fluorotelomer alcohols (FTOHs)	6:2 FTOH	647-42-7	ND to 135 000	(1)
	8:2 FTOH	678-39-7	0.36 to 117 000	(1, 13)
	10:2 FTOH	865-86-1	ND to 117 000	(1)
Fluorotelomer acrylates (FTACrS)	8:2 FTACr	27905-45-9	ND to 47.7	(13-15)
	10:2 FTACr	17741-60-5	ND to 17.4	(14, 15)
Fluorotelomer methacrylates (FTMACrS)	6:2 FTMACr	2144-53-8	ND to 13.0	(16)
Fluoroalkyl sulfonamides (FASAs)	N-Methyl perfluorobutane sulfonamide (MeFBSA)	68298-12-4	0.3 to 3.4	(14)
	Perfluorooctane sulfonamide (FOSA)	754-91-6	ND to 1.3	(17, 18)
	N-Ethyl perfluorooctane sulfonamide (EtFOSA)	4151-50-2	ND to 0.9	(16-19)
	N-Methyl perfluorooctane sulfonamide (MeFOSA)	31506-32-8	ND to 0.8	(16-19)
Fluoroalkyl sulfonamido ethanols (FASEs)	N-Methyl perfluorobutane sulfonamido ethanol (MeFBSE)	34454-97-2	0.6 to 141	(14)
	N-Ethyl perfluorooctane sulfonamido ethanol (EtFOSE)	1691-99-2	ND to 7.7	(16-19)
	N-Methyl perfluorooctane sulfonamido ethanol (MeFOSE)	24448-09-7	ND to 9.5	(15, 18, 19)
Perfluoroalkyl carboxylic acids (PFCAs)	Perfluorobutanoic acid (PFBA)	375-22-4	ND to 2.9	(1)
	Perfluoropentanoic acid (PFPeA)	2706-90-3	ND to 439	(1)
	Perfluorohexanoic acid (PFHxA)	307-24-4	ND to 7.9	(1, 16)
	Perfluorooctanoic acid (PFOA)	335-67-1	ND to 9.5	(1, 16, 18)
	Perfluorononanoic acid (PFNA)	375-95-1	ND to 3.5	(1, 16, 18)
	Perfluorodecanoic acid (PFDA)	335-76-2	ND to 2.2	(1, 16)
Perfluoroalkane sulfonic acids (PFASAs)	Perfluorobutane sulfonic acid (PFBS)	375-73-5; 59933-66-3	ND to 0.90	(1, 16)
	Perfluoropentane sulfonic acid (PFPS)	2706-91-4	ND to 0.27	(18)
	Perfluorohexane sulfonic acid (PFHxS)	355-46-4	ND to 0.59	(1, 16, 18)
	Perfluorooctane sulfonic acid (PFOS)	1763-23-1	ND to 1.8	(1, 16, 18)
	Perfluorodecane sulfonic acid (PFDS)	335-77-3	0.0009 to 0.0019	(20)
Polyfluoroalkyl phosphoric acid esters (PAPs)	6:2 diPAP	57677-95-9	ND to 0.094	(1)
	8:2 diPAP	678-41-1	ND to 0.031	(1)

just the gas phase, some to just the particle phase, and some methods sample both the gas and particle phases together (defined as total air in Table 4). Selecting a sampling method should account for the expected phase and the analyte chemical

properties in the phase of interest. In addition, for methods that delineate the difference between gas and particle phases, the size cutoff for particle sampling should be understood, considered, and reported.

TABLE 3 Passive Sampling Methods for PFAS in Air: Advantages and Disadvantages

Sampling Media	Targeted Phase	Targeted Species	Time of Deployment	Published Equivalent Sampling Rates or Volumes	Commercially Available	Shipping and Storage Considerations	References	Notes
Polyurethane foam (PUF) disks	Gas phase and some particulate matter (PM)	FTOHs, FOSEs, EtFOSEA, PFSAAs, PFCAs	17 days to 120 days	Yes	Yes; some assembly required	Samples wrapped in Al foil; stored at -18 °C	(20, 28, 2, 29)	Not recommended for FTOHs (2)
Sorbent-impregnated PUF (SIP) disks	Gas phase	FTOHs, FTACrs, FASEs, FASAs, FTACrs, FTMACrs, PFSAAs, (C4-C10), PFCAs (C4-C10)	14 days to 83 days	Yes	No; assembly challenging	Kept at -20 °C (14); stored in airtight Al-lined jars at -21 °C, shipped in cooler (16)	(14, 16, 18, 19, 20, 2)	Direct sunlight to be avoided (14); some uptake data derived from outdoor samplers (16)
Activated carbon fiber felts (ACFs)	Gas phase and PM	FTOHs, 8:2 FTACr, 8:2 FTMACr	7 days to 21 days	Yes	Yes; some assembly required	Storage in polyethylene bags, kept at -30 °C	(13)	No details about sampler construction provided
Polyethylene (PE) sheets	Gas phase and PM	FTOHs, FTACrs, FASAs, FASEs	14 days to 28 days	Yes	Yes; some assembly required	Kept at -20 °C until analysis	(30)	No details about sampler construction provided
Glass or quartz fiber filters (GFFs or QFFs)	PM	FTOHs, FTACrs, FASAs, FASEs, PFCAs, PFSAAs, FTUCAs, HFPO-DA	17 days	Limited	Yes; minimal assembly required	Kept at -20 °C until analysis	(29)	Sampling in occupational indoor setting

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7.3 Existing approaches to airborne sampling for PFAS can be divided into three major approaches: active sorbent sampling, passive sorbent sampling, and online sampling. Both active and passive sorbent approaches are usually applied as “offline” methods, that is, a sample is first collected and then brought to a laboratory for analysis. However, “online” sampling and analysis methods, where a sample is actively collected and immediately analyzed, are becoming more common. Online PFAS measurement strategies are discussed in 7.9.

7.4 Active sorbent sampling draws air through a sorbent sampler using a downstream pump. Passive sorbent sampling exposes a sorptive sampling media to the air and relies on diffusion of target PFAS compounds onto the sampler.

7.4.1 Passive samplers (7.6) are relatively easy to deploy, use, and are often less expensive than active sampling, but they can have limited analyte applicability and concentration ranges. To use passive samplers, a compound- and sampling media-specific sampling rate must be known to calculate concentrations in air; however, these sampling rates may also vary depending on the sampler design and environmental conditions (21). Sorbents for PFAS passive sampling are typically extracted in liquids prior to analysis.

7.4.2 Active sampling methods collect PFAS at a higher rate and over a shorter time than passive sampling. For active sampling sorbent-based techniques, the breakthrough volume needs to be determined for each PFAS/sampling media com-

ination. Active sampling apparatuses are of relatively higher cost than passive samplers, can require pump calibration, and require training to deploy. Active sampling sorbents can either be extracted by liquids (7.7) or thermally (7.8).

7.5 For samples collected onto sorptive media, manufacturer storage and handling recommendations should be followed, if available. Storage temperatures of 4 °C to -30 °C have been reported in the literature for samples collected using this type of media. Further details can be found in Table 3 and Table 4. Generally, it is recommended to keep the time between sampling and analysis as short as possible. When ready for analysis, the PFAS on sorptive media are then desorbed (extracted) into a liquid, gas, or secondary sorbent phase using techniques described in Section 8 and analyzed using instrumentation described in Section 9.

7.6 *Passive Sorbent Sampling for Liquid Extraction*—During passive sorbent sampling, sorbent media are exposed to ambient or indoor air environments. Two types of passive samplers are typically used: those operating in the linear uptake range and those acting as equilibrium samplers. Depending on the sampling regime and compounds of interest, passive sampling sorbents vary in material, shape, and design. Widely used polyurethane foam (PUF) passive samplers are typically disc-shaped with a diameter of roughly 15 cm and a thickness of about 1 cm, but other sorbents have also been used, including some in porous containers. For example, rectangular

TABLE 4 Active and Online Sampling Methods for PFAS in Air: Advantages and Disadvantages

Sampling Media	Targeted Phase	Targeted Species	Time of Deployment	Typical Volumes	Commercially Available	Shipping and Storage Considerations	References	Notes
Polyurethane foam (PUF)	Total air or gas phase only	SVOC PFAS only EtFOSE, MeFOSE, MeFOSEA	hours to days	100's m ³	Yes	NA	(21, 31)	Large extraction volumes needed; pre-cleaning of PUF may be necessary
PUF-NPSDBR-PUF sandwich cartridges	Total air or gas phase only	Wide analyte range – FTOHs, FTACrS, FASEs, FASAs	hours to days	m ³ to 100's m ³	Yes	Wrap in clean aluminum foil, place in sealed plastic zipper bag, and store at -15 °C	(15, 21, 32-33)	Large extraction volumes needed, high and low volume sampling possible
NPSDBR	Total air or gas phase only	Wide analyte range – FTOHs, FTACrS, FASEs, FASAs	hours	m ³ to 10's m ³	Yes	Store at -20 °C	(21, 30)	Can be packed in different types of high- or low-volume sampling cartridges
Solid-phase extraction (SPE) cartridges	Total air or gas phase only	FTOHs, FASAs, and FASEs by GC-MS PFCAs (C4 to C12), PFASs (C4 to C8), FTUCAs, diPAPs by HPLC-MS/MS	up to 24 h	m ³ to 100 m ³	Yes	Wrap in clean aluminum foil, place in sealed plastic zipper bag, and store at -20 °C	(1, 34, 35)	Depending on sorbent, various PFAS groups can be targeted
Glass or quartz fiber filters (GFFs or QFFs)	Particle phase only	PFCAs, PFASs, FTUCAs, PFOSA, and 6:2 FTS by LC-MS/MS FTOHs, FASAs, FASEs, and fluorotelomer olefins (FTOs) by GC-MS	hours to days	10's m ³ to 100's m ³	Yes	Place in clean aluminum foil, place in plastic zipper bag or plastic petri slides, or both, store at 4 °C to -20 °C	(36-40)	Can be used with multi-stage impactors, denuders, or to collect specific particle sizes (for example, PM2.5 or PM10) or to remove particles for gas-phase only sampling. Pre-treatment (baking) of filters is necessary
Thermal desorption (TD) tubes	Total air or gas phase only	PFCAs, FTOHs, FTACrS, FOSEs, FOSAs, FASEs, and FASAs, MeFOSE, MeFOSEA	minutes to days	mL to 100's L	Yes	Seal with brass storage caps, analysis should be carried out within 1 month	(41-43, 44, 45) ^A	Tubes are reusable, no extraction needed, samples can be split and saved (re-collected) for re-analysis at a later time
Chemical Ionization Mass Spectrometry (CIMS)	Total air or gas phase only	FTOHs, FTACrS, PFCAs, PFASs, FTUCAs, diPAPs	seconds to minutes	NA	Yes	Instrument must be transported to and from the sampling location in most cases	(26, 27)	Direct measurement with no sample preparation, no isomeric information. Expensive and requires trained operator

^A See also proposed ASTM Standard: Test Method for Determination of Fluorotelomer Alcohols in Air by Thermal Desorption Gas Chromatography/Tandem Mass Spectrometry.

polyethylene (PE) sheets have been used as equilibrium samplers (~10 cm wide, ~40 cm long, and 25 μm or 50 μm thick) without housing to sample PFAS in indoor air. The passive sampler is delivered to the sampling location in a sealed sample container. The sample container is then opened at the start of the sampling period. The analyte of interest moves either across or around the housing containing the sorbent (if present) or directly to the sorbent via existing air movement. The analyte then migrates into the sorbent material by diffusion. Most sorbent housings are constructed of stainless steel or plastic, while transport containers are typically made of plastic if PFAS are targeted. Passive PFAS sampling events typically last for 14 days to 60 days, after which the sorbent material is sealed in a transport container and returned to a laboratory for extraction and analysis. As reported to date, liquid extraction methods are most commonly used for passive PFAS sampling sorbents. While there is nothing fundamentally preventing passive sampling via thermal desorption for PFAS, very few relevant compounds have been tested to date. Therefore, this option is excluded from this guide for the time being.

7.6.1 A range of sorbents have been used in passive PFAS samplers. Commercially available media samplers include: PUF disks, activated carbon fiber felts (ACFs), PE sheets, and glass or quartz fiber filters (GFFs or QFFs). Sorbent-impregnated PUF (SIP) disks have also been used but are currently not commercially available. Usually, a nonionic polystyrene divinylbenzene resin (NPSDBR) is used as sorbent to impregnate PUF disks for passive sampling. Commercially available products may be more reproducible than samplers that are not commercially available. Each sorbent material has only been evaluated for a limited number of PFAS (see targeted species in Table 3). Chemical-specific performance testing for each sorption media must be completed prior to using the media beyond previously tested PFAS.

7.6.2 To quantify the PFAS concentration in air using passive samplers, an effective air sampling rate must be calculated for the sampling device operating in the linear uptake range, or the equilibrium partition coefficient needs to be known (at the temperature of deployment). The sampling rate is a function of the housing design, sorbent, and environmental conditions. A review by Melymuk et. al. (21) demonstrated that sampling rates for passive samplers can vary from $0.02 \text{ m}^3 \text{ s}^{-1}$ to $20 \text{ m}^3 \text{ s}^{-1}$ and may be compound-specific. While the passive sampling rate is not critical for screening sampling objectives, it is critical to determining accurate air concentrations. For accurate quantification, the air sampling rate needs to remain constant throughout the sampling period. For reference, non-linear uptake to passive samplers has been shown for polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) after six to nine weeks (22). Different sorbent media have different linear uptake durations and should only be compared for time periods when both are in the linear uptake range.

7.6.3 When outside ambient air passive sampling is performed, air temperature ($0 \text{ }^\circ\text{C}$ to $20 \text{ }^\circ\text{C}$) and wind speed (1.5 m s^{-1} to 3 m s^{-1}) have been shown to affect the linear uptake duration by factors of two or more for PCBs and PAHs

(uptake rate under these conditions is unknown for PFAS) (22). However, in most indoor environments, temperatures and air speeds vary within a much narrower range and therefore, these variations will not have as big an effect on the sampling rate as outdoors. However, even these small variations in indoor temperature and air speed should be considered when choosing sampling locations and designs for passive samplers. For example, the samplers should be positioned in a way that drafts from open windows or doors as well as strong direct sunlight are avoided. At the same time, air flow directly near and across the passive sampler should not be hindered by objects or walls.

7.6.4 Uptake or deposition, or both, of particles must be considered when deploying passive samplers. The sampler housing should protect the sampling media from deposition of large particles without restricting air movement. Diffusion of small particles into the sampler may still be an issue; low-density PUF samplers may be especially susceptible to accumulating particles (21). SIP disks are generally considered gas-phase only samplers (21). To determine the extent of the influence of particles on the sampling results, passive sampler calibration against active samplers can provide valuable insights (21).

7.6.5 Diffusive uptake data, in particular equivalent sampling rates, sampling volumes, and sampler-air partitioning coefficients, can be found in the literature for different passive sampling media and for a broad range of PFAS. For example, Shoeib et al. (2) provide measured partition coefficients, mass-transfer coefficients, and sampling rates for several neutral PFAS for passive samplers using PUF or SIP disks. Karaskova et al. (20) tested passive samplers with PUF disks indoors and outdoors, and determined PUF-air partition coefficients ($K_{\text{PUF-air}}$) for PFSAs, PFCAs, and FOSAs/FOSEs based on octanol-air partition coefficient data. The resulting log ($K_{\text{PUF-air}}$) values ranged from -0.5 for PFBA to 1.7 for PFTA (20). Goosey and Harrad (17) measured sampling rates for SIP disks using a part-sheltered (indoor) housing configuration of their passive samplers as well as a fully sheltered (outdoor) housing configuration. The indoor sampling rates ranged from $0.8 \text{ m}^3 \text{ day}^{-1}$ for PFOS to $2.4 \text{ m}^3 \text{ day}^{-1}$ for MeFOSA; the PFAS included were PFOS, PFOA, PFHxS, MeFOSA, EtFOSA, FOSA, MeFOSE, and EtFOSE (17). Additional information on equivalent sampling rates or volumes for each type of passive sampling media is summarized in Table 3 and details can be found in the references therein.

7.6.6 It must be noted that the uptake data varies with the chemical species, the sampler housing design, and indoor conditions. It may also vary with the density of the sampling media, for example, not all PUF disks have the same density and therefore their uptake of PFAS will vary. Outdoor passive sampler uptake data may not apply to indoor passive samplers, because wind and weather conditions outdoors may result in very different sampling rates (17, 21). Calibration of passive samplers or at least comparison of air concentrations obtained by passive sampling to active sampling data for quality control is recommended.

7.7 *Active Sorbent Sampling for Liquid Extraction*—In active air sorbent sampling, air containing PFAS is drawn through a sorbent using a pump. For that purpose, a pump set

to a specific, known flow is connected to a sampling device. Knowledge of the sampling flow rate and duration allows the total sampling volume to be determined. Hence the concentration of an analyte in air can be calculated in a more direct manner than compared to passive sampling. Sampling times are also often much shorter (hours to days) than for passive sampling (days to weeks). Increased noise from the pump as well as the need for a power supply for extended pump operation beyond the 24 h typically provided by batteries are limitations to consider for sorbent-based active sampling. It must be ensured that all the applied sampling equipment, including pumps, tubing, cartridge housing, and sampling media, are appropriate for the sampling environment and conditions.

7.7.1 Sampling media used for active sampling with liquid extraction are similar to those used for passive sampling (Table 4). Common media consist of cartridges containing PUF plugs or NPSDBR resin sandwiched between two PUF plugs. Both types of cartridges are commercially available. The cartridge housings are usually made of glass. Different types of solid-phase extraction (SPE) cartridges, commercially available and self-packed versions, have been used for active PFAS sampling. SPE cartridge housings are often made of polypropylene. The specific sampling media in the SPE cartridges corresponds to the targeted PFAS species and intended analytical method. As for passive sampling, chemical-specific performance testing for each media must be completed prior to using a particular sampler.

7.7.2 Depending on the flow rate, active sampling using sorbents that require liquid extraction can be classified as either low volume ($<3 \text{ m}^3 \text{ h}^{-1}$ to $5 \text{ m}^3 \text{ h}^{-1}$) or high volume ($15 \text{ m}^3 \text{ h}^{-1}$ to $80 \text{ m}^3 \text{ h}^{-1}$), with corresponding lower or higher total sampling volumes (21). High-volume sorbent samplers have a typical total sampling volume of about 600 m^3 , while low-volume sorbent samplers process about 100 m^3 of air or less. The size or mass of the sampling media must be matched to the sampling flow rate and expected total sampling volume. Sampling durations for active sorbent sampling can vary from several hours to a month (21); however, longer sampling can lead to breakthrough. Breakthrough is defined as the volume of a known atmosphere that can be passed through the sorbent sampler before the concentration of the vapor eluting from the tube reaches 5 % of the applied test concentration (adapted from Practice D6196). If breakthrough is a concern, especially for more volatile PFAS, the degree of breakthrough must be determined and considered. Another potential problem with long sampling durations for sorbent sampling is the collection of large amounts of unwanted chemicals in the sampling media that may complicate extraction or analytical measurements, or both.

7.7.3 Sorbent breakthrough has been evaluated for PUF-NPSDBR-PUF sandwich and SPE cartridges. Shoeib et al. (2) compared concentrations of FTOHs, FOSAs, and FOSEs in the front PUF plug to those in the back PUF plug in a PUF-NPSDBR-PUF sandwich cartridge, using a sampling volume of $\sim 300 \text{ m}^3$. They found $\sim 40 \%$ of the FOSAs in the back PUF plug, but only $<8 \%$ of the FOSEs. They also determined that $>95 \%$ of FTOHs were present in the NPSDBR and not in the

PUF plugs. If another NPSDBR cartridge was put in line downstream of the PUF-NPSDBR-PUF sandwich cartridge, 30 % breakthrough of 6:2 FTOH was observed at a sampling volume of 60 m^3 , but no other analyte was detected in the second cartridge (2). Huber et al. (3) measured breakthrough of PUF-NPSDBR-PUF sandwich cartridges using analyte spikes at two different concentrations. They saw 36 % to 73 % breakthrough of 4:2 FTOH, $<13 \%$ breakthrough of 6:2 FTOH, $<2 \%$ breakthrough of 8:2 FTOH, 10:2 FTOH and FOSEs, and no breakthrough of FOSAs. Yao et al. (1) used a similar approach to assess breakthrough of PFAS sampled with SPE cartridges. No breakthrough for any of the FTOHs, FOSEs, or FOSAs at either spike amount was observed, but low ($<1 \%$) breakthrough was measured at the low spike amount (10 ng , 5 m^3 sampling volume) for PFBA, PFHpA, PFNA, and 8:2 diPAP. In summary, the more volatile chemicals show higher breakthroughs during active sampling.

7.7.4 Particle-phase sampling on QFFs or GFFs is possible using active sampling. If particulates are the target of the sampling effort, the particle-size cut-off should be determined based on the sampling flow rate and orifice diameter. It should be further determined to what degree, if any, PFAS in the gas phase adsorb to the filter during sampling, because this effect may distort particle phase results (23).

7.7.5 Filters may also be used to remove the particle phase prior to gas-phase sampling. The extent at which the filter is capturing gas-phase PFAS should also be determined (23).

7.8 *Active Sorbent Sampling for Thermal Extraction*—Once collected on thermal desorption (TD) tubes, this approach uses heat and flow of inert gas for transferring analytes from a TD tube to a gas chromatograph. This approach does not require solvent extraction of sample media before analysis. When performing sampling prior to thermal desorption, tubes containing a suitable, TD-compatible sorbent type or series of sorbents has to be selected for the class and volatility of the PFAS to be sampled. When suitable sorbents are chosen, the PFAS compounds are retained by the sorbent tube(s) and removed from a flowing air stream. Sorbents for thermal desorption can be separated into three common classes: porous polymers, which are typically weak sorbents (that is, 2,6-diphenyl-p-phenylene oxide, DPPO, etc.); graphitized carbon sorbents, which span from weak to medium strength; and carbonized molecular sieves, which are strong sorbents. If multiple sorbents of different strength are used, the sorbents are arranged in order of increasing sorbent strength within the tube. By ensuring the weaker sorbent is in front of stronger sorbent during sampling, irreversible adsorption of higher boiling compounds on the stronger sorbents is prevented. The tube itself can be made from glass or stainless steel, with stainless steel being most common as it is more robust than glass and will not break if mishandled.

7.8.1 Typical flow rates for sampling onto sorbent tubes range from 20 mL min^{-1} to 200 mL min^{-1} (Practice D6196). Air volumes sampled typically range between 20 L to 500 L for detection of PFAS. Higher volumes and flow rates up to 500 mL min^{-1} can be used for lower volatility chemicals, but breakthrough volumes for the target compounds should be determined prior to field studies being conducted. In addition,