PFAS Roadmap: What MWF Producers and Users Need to Know Now

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"The times, they are a changin'…" - Bob Dylan

PFAS Roadmap: Outline

- Introduction (brief!)
- Regulatory environment changing rapidly
- Where do I look for PFAS? Do I need to look?
- How do I analyze for PFAS?
  - and do we need a special method for lubricants?
- And what do I do if I find PFAS?

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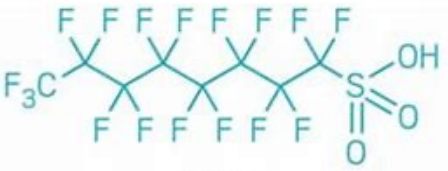
PFAS Roadmap: Introduction

- Called “Forever Chemicals,” just what are they?
  - Principle groupings: perfluoro alkyl substances; polyfluoro alkyl substances; fluoropolymers; polymeric perfluoropolyethers
  - Examples: perfluorooctanic sulfonic acid (PFOS) perfluorooctanoic acid (PFOA)

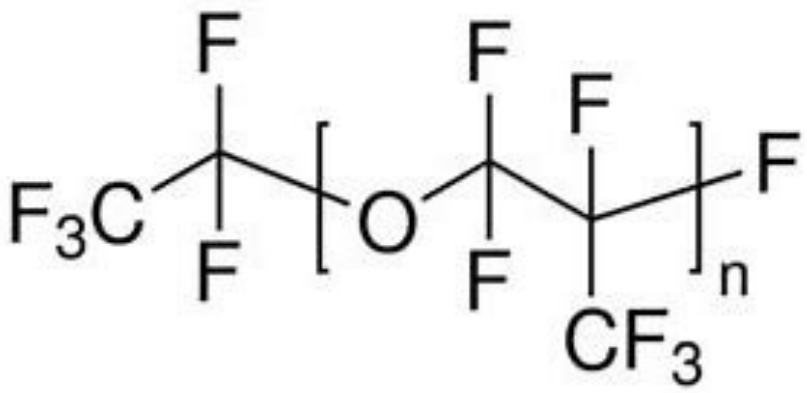


PFOS

PFOA

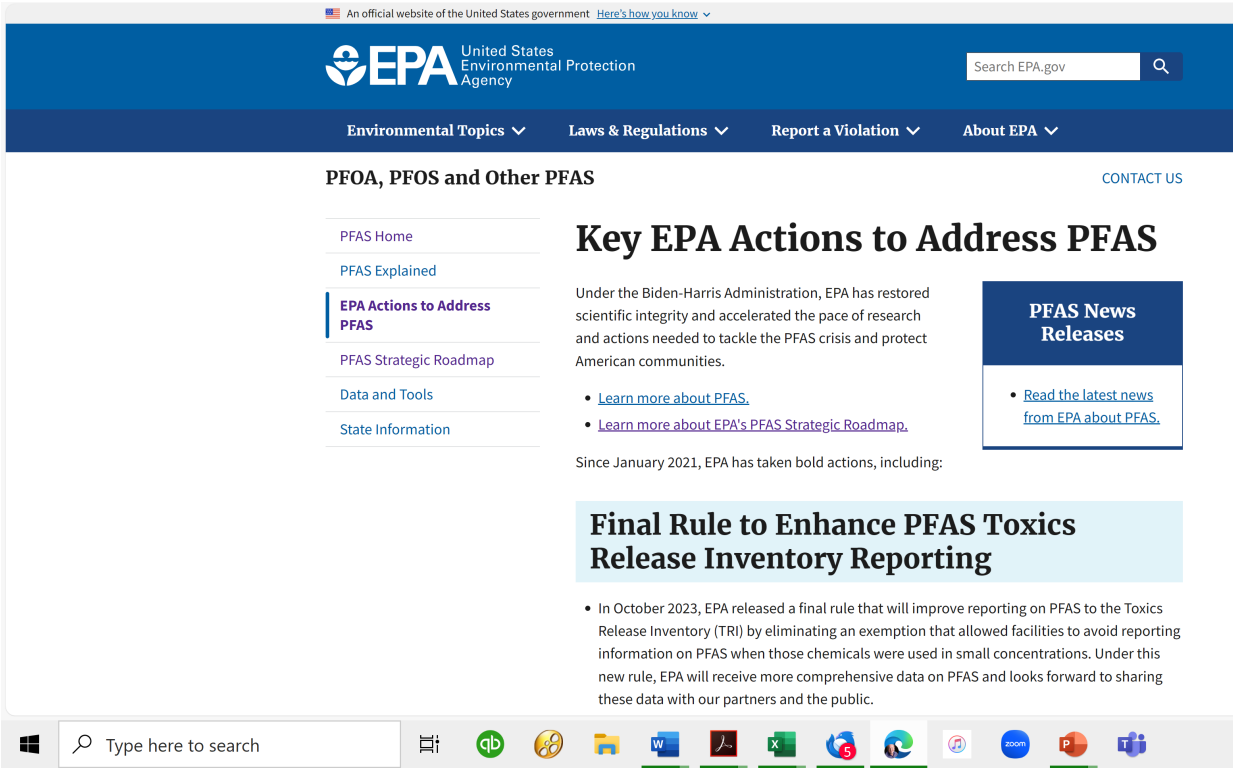
PFAS Roadmap: Introduction

- But the group also includes fluoropolymers such as Teflon® (tetrafluoropolyethylene), Viton® (polymer of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene) and Krytox® (polyhexafluoropropyleneoxide)
  - ® trademark of The Chemours Company



PFAS Roadmap: Regulatory

Regulatory environment changing rapidly:



Key EPA Actions to Address PFAS | US EPA

PFAS Roadmap: Regulatory

Resources:

- Key EPA actions: Key EPA Actions to Address PFAS | US EPA
- PFAS Analytical Tools: PFAS Analytic Tools | ECHO | US EPA
- PFAS Analytical Methods: PFAS Analytical Methods Development and Sampling Research | US EPA
- Wisconsin: PFAS | Wisconsin DNR

PFAS Roadmap: Regulatory

An official website of the United States government Here's how you know

United States Environmental Protection Agency

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Water Research

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- Water Research Grants
- Research Outputs
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PFAS Analytical Methods Development and Sampling Research

Per- and polyfluoroalkyl substances (PFAS) are a large class of synthetic chemicals that present numerous analytical challenges, including their widespread presence in a variety of environmental samples, occurrence of isomers for some compounds, and precursor transformations that may occur during preservation and storage of the samples. EPA's methods for analyzing PFAS in environmental media are in various stages of development and validation.

EPA scientists are developing validated analytical methods for drinking water; groundwater; surface water; wastewater; and solids, including soils, sediments, biota, and biosolids, which may eventually become standard methods or research methods. Visit EPA's status of PFAS research and development webpage to get updates about this and other PFAS research.

Information on this Page

- Standard Analytical Methods
- Research Analytical Methods
- Other Federal Analytical Methods
- Sampling
- Data Analysis
- Laboratory Certification

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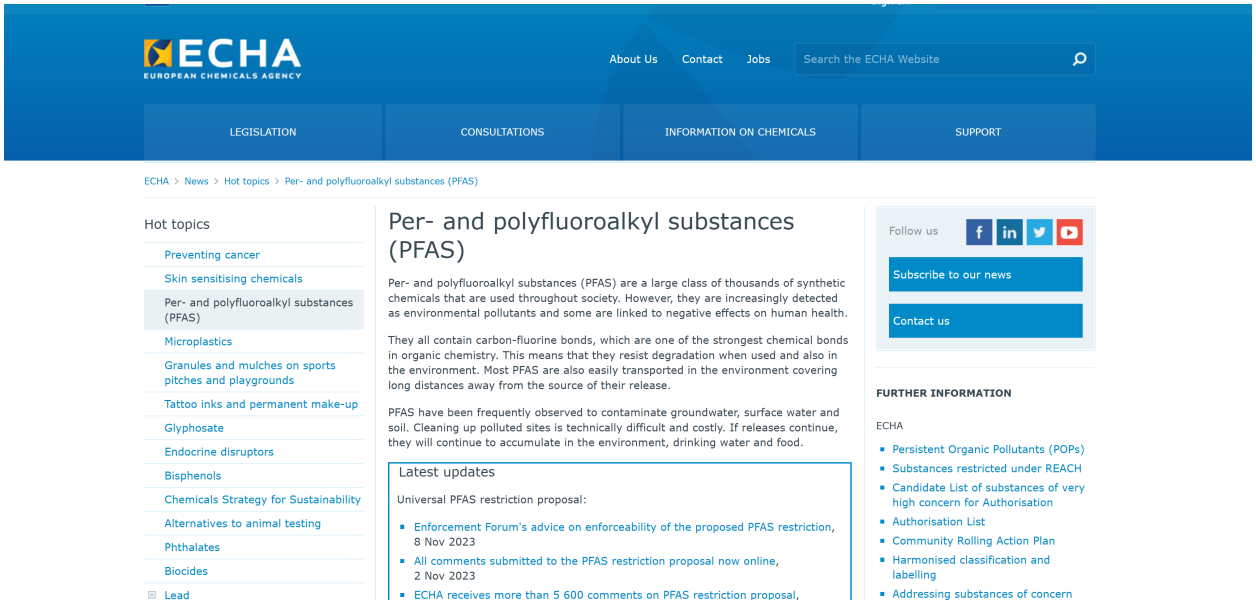
PFAS Roadmap: Regulatory

Regulatory environment changing rapidly:



[Per- and polyfluoroalkyl substances (PFAS) - ECHA (europa.eu)]

Where Do I Look for PFAS?

- In my plant?
- In my raw materials?
- In my water?
- In indoor air?

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How Do I Analyze for PFAS?

- Here's where it gets tricky (and potentially expensive)…
- US EPA is leading methods development
  - PFAS Analytical Methods Development and Sampling Research | US EPA
- Methods are available for drinking water, waste water and soil and for air, but not for lubricants, at least not yet…

How Do I Analyze for PFAS?

- In order to determine if I have a problem, an analytical method being developed by EPA, Total Organic Fluorine, is the suggested starting point

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How Do I Analyze for PFAS?

- For lubricants, closest method available is EPA Analytical Chemistry Branch (ACB) Method B21-02, Analysis of PFAS in an Oily Matrix

- But…it's not validated for lubricants

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ACB Method B21-02

Oily samples are passed through a Florisil solid phase extraction (SPE) cartridge and the oily matrix is washed off the SPE by a mixed solvent of hexane and ethyl acetate (9/1, v/v). The PFAS compounds are eluted from the SPE with methanol/acetone mixture (9/1, v/v). The collected eluate samples are concentrated and analyzed with a liquid chromatography tandem mass spectrometer (LC-MS/MS). The instrumental analysis of samples with LC-MS/MS follows the analysis described in EPA Method 537.1. Isotopically labeled internal standards are used for quantitation. Isotopically labeled extraction standards are added prior to sample processing and the recoveries from each sample are monitored.

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ACB Method B21-02

NOTE: This method was validated at ACB using a clean oil matrix. When analyzing a product formulated in oil, petroleum distillates, or mineral oils, matrix interference is expected. Therefore, it is recommended that any detection of PFAS at low levels (around or below 10 times the reported limits of quantitation) be confirmed using different analytical techniques. Otherwise, the compound(s) should be reported as "tentatively identified." The ACB relies on a high resolution accurate mass (HRAM) Mass Spectrometer coupled with liquid chromatography (LC-MS) for confirmation.

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ACB Method B21-02

APPENDIX I -

CHEMICAL ABSTRACTS SERVICE (CAS) REGISTRY NUMBERS and CHEMICAL NAMES

Analyte	CAS #	Name
PFBA	375-22-4	Perfluorobutanoic Acid
PFBS	375-73-5	Perfluorobutanesulfonic Acid
PFPeA	2706-90-3	Perfluoropentanoic Acid
PFPeS	2706-91-4	Perfluoropentanesulfonic Acid
PFHxA	307-24-4	Perfluorohexanoic Acid
PFHxS	355-46-4	Perfluorohexanesulfonic Acid
PFHpA	375-85-9	Perfluoroheptanoic Acid
PFHpS	375-92-8	Perfluoroheptanesulfonic Acid
PFOA	335-67-1	Perfluorooctanoic Acid
PFOS	1763-23-1	Perfluorooctanesulfonic Acid
PFNA	375-95-1	Perflurononanoic Acid
PFNS	68259-12-1	Perfluorononanesulfonic Acid
PFDA	335-76-2	Perfluorodecanoic Acid
PFDS	335-77-3	Perfluorodecanesulfonic Acid
PFUdA	2058-94-8	Perfluoroundecanoic Acid
PFDoA	307-55-1	Perfluorododecanoic Acid
PFDoS	79780-39-5	Perfluorododecanesulfonic Acid
PFTrDA	72629-94-8	Perfluorotridecanoic Acid
PFTeDA	376-06-7	Perfluorotetradecanoic Acid
PFHxDA	67905-19-5	Perflurohexadecanoic Acid

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ACB Method B21-02

Table 1. ACB Method Validation Study Results -
Summary of the recoveries of selected PFAS compounds and their labeled extraction standards from a fortified oil matrix at different concentration levels

Targeted PFAS compounds

Average recoveries (%) from each fortification level

Analyte	*0.025 ppb*	*0.050 ppb*	*0.126 ppb*	*0.630 ppb*	*Average*
PFBA	24%	51%	31%	71%	44%
PFBS	211%	201%	120%	139%	168%
PFPeA	80%	59%	30%	58%	57%
PFPeS	25%	33%	80%	107%	61%
PFHxA	0%	62%	61%	60%	45%
PFHxS	119%	118%	147%	175%	140%
PFHpA	101%	94%	65%	65%	81%
PFHpS	69%	74%	95%	120%	90%
PFOA	61%	50%	162%	157%	107%
PFOS	82%	90%	127%	110%	102%
PFNA	73%	80%	68%	61%	71%
PFNS	96%	97%	178%	136%	127%
PFDA	87%	94%	91%	101%	93%
PFDS	116%	121%	215%	224%	169%
PFUdA	80%	84%	136%	162%	115%
PFDoA	85%	97%	154%	216%	138%
PFDoS	109%	117%	219%	210%	164%
PFTrDA	69%	79%	149%	148%	111%
PFTeDA	80%	95%	140%	152%	117%
PFHxDA	122%	146%	133%	178%	145%
PFODA	158%	169%	398%	382%	277%
FOSAA	41%	65%	153%	104%	91%

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ASTM

Designation: E3302 – 22

Standard Guide for PFAS Analytical Methods Selection[1]

This standard is issued under the fixed designation E3302; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide discusses the selection and application of analytical methods and techniques used to identify and quantitate per- and polyfluoroalkyl substances (PFAS) in environmental media. This guide provides a flexible, defensible framework applicable to a wide range of environment programs. It is structured to support a tiered approach with analytical methods, procedures, and techniques of increasing complexity as the user proceeds through the evaluation process. This guide addresses key decision criteria and best practices to aid users in achieving project objectives. There are numerous technical decisions that must be made in the selection and application of analytical methods and techniques used during environmental data acquisition programs. It is not the intent of this guide to define appropriate technical decisions, but rather to provide technical support within existing decision frameworks.

1.2 This guide informs practitioners on the considerations relevant to the selection and application of analytical methods and techniques for the quantitative and qualitative determination of PFAS in a variety of environmental sample media. This guide encourages user-led collaboration with stakeholders, including analytical laboratories, data evaluation practitioners, and regulators, in the selection and application of analytical methods and techniques used to support project-specific decision criteria and objectives as applied within a particular environmental regulatory program. This guide recognizes the complexity and diversity of environmental programs and project objectives and provides technical support for a range of project applications.

1.3 This guide is intended to complement, not replace, than 4 700 Chemical Abstracts Service (CAS)-registered substances. Environmental concerns pertaining to PFAS are centered primarily on the perfluoroalkyl acids (PFAA), a subclass of PFAS, which display extreme persistence and chain-length-dependent bioaccumulation and adverse effects in biota.

1.5 This guide recognizes that published analytical methods performed by commercial laboratories are limited to determination of a small subset of the more than 4 700 CAS-registered PFAS.

1.6 The goal of this guide is to provide a technical framework for informed selection and application of analytical methods and techniques for the determination of target and non-target PFAS in environmental sample media.

1.7 This guide aids users in selecting PFAS analytical methods for various environmental applications.

1.8 This guide discusses existing published analytical methods for quantitative determination of method-specific lists of target analytes, as well as non-standard analytical approaches developed to qualitatively determine a broader range of PFAS, for a variety of environmental applications. This guide also provides an overview of research trends in this rapidly developing field.

1.9 This guide discusses the challenges and limitations of analytical methods and techniques in the detection and quantitation of the large, complex set of PFAS.

1.10 This guide describes widely accepted considerations and best practices used in the selection and application of analytical procedures used during PFAS environmental programs. This guide complements but does not replace existing technical guidance and regulatory requirements.

ASTM

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:*[2]

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)

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)

2.2 *USEPA Documents:*[3]

EPA QA/G-4 Guidance on Systematic Planning Using the Data Quality Objectives Process, February 2006

EPA/600/F-17/022e PFAS Methods and Guidance for Sampling and Analyzing Water and Other Environmental Media – Technical Brief, February 2019, EPA/600/F-17/022h, updated January 2020

USEPA 815-B-16-021 Technical Advisory – Laboratory Analysis of Drinking Water Samples for Perfluorooctanoate (PFOA) Using EPA 537 Rev. 1.1, September 2016

USEPA Method 537 Version 1.1 Determination of Selected Perfluorinated Alkyl Acids (PFAAs) in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

USEPA Method 537.1 Version 2.0 Determination of Selected Per- and Polyfluorinated Alkyl Substances (PFAS) in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

USEPA Method 533 Determination of Per and Polyfluoro-

PFAS Substances. CompTox Chemistry Dashboard, Last updated September 16, 2020, Online, Available: https://comptox.epa.gov/dashboard/chemical_lists/PFASMASTER

U.S. Environmental Protection Agency Drinking Water Health Advisories for Perfluorooctanoate (PFOA) and Perfluorooctane Sulfonate (PFOS), 822-R-16-004, 2016

U.S. Environmental Protection Agency Lifetime Health Advisories and Health Effects Support Documents for Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS), Federal Register, Vol 81, No. 101, May 25, 2016

2.3 *ISO Documents:*[4]

ISO 25101 Determination of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) in Water – Method for Unfiltered Samples Using Solid Phase Extraction and Liquid Chromatography / Tandem Mass Spectrometry (LC-MS/MS)

ISO 21675 Determination of Polyfluorinated Alkyl Substances (PFAS) in Water – Method Using Solid Phase Extraction and Liquid Chromatography / Tandem Mass Spectrometry (LC-MS/MS)

3. Terminology

3.1 *Definitions:*

3.1.1 *adsorbable organofluorine (AOF), n*—a fraction of organofluorine that will sorb to a particular media, for example carbon, and that remains sorbed to the media after removal (washing) of the inorganic fluoride.

3.1.2 *combustion ion chromatography (CIC), n*—a technique that combines pyrolysis of a sample and analysis of the combustion products using ion chromatography.

3.1.3 *extractable organofluorine (EOF), n*—the fraction of organic fluorine that is first extracted and then analyzed.

3.1.4 *fluoride ion, n*—the inorganic anion of fluorine (F^-); that is, fluoride.

ASTM

USEPA Method 537 Version 1.1 Determination of Selected Perfluorinated Alkyl Acids (PFAAs) in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

USEPA Method 537.1 Version 2.0 Determination of Selected Per- and Polyfluorinated Alkyl Substances (PFAS) in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

USEPA Method 533 Determination of Per-and Polyfluoroalkyl Substances (PFAS) in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), Revision July 2021

USEPA Test Method 8327 Per-and Polyfluoroalkyl Substances (PFAS) Using External Standard Calibration and Multiple Reaction Monitoring (MRM) Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

USEPA Draft Method 1633 Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS, EPA 821-D-21-001, August 2021.

U.S. Environmental Protection Agency PFAS Master List of

[2] 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.

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

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3.1.4 *fluoride ion, n*—the inorganic anion of fluorine (F^-); that is, fluoride.

3.1.5 *fluorides, n*—any compound containing fluorine are categorically deemed fluorides.

3.1.6 *fluorine (F), n*—a chemical element, diatomic form (F2); it is a highly toxic gas, reactive, and yellow-green in color.

3.1.7 *liquid chromatography mass spectrometry / mass spectrometry (LC/MS/MS; also known as triple quadrupole or triple quad LC/MS), n*—an analytical instrument that laboratory methods use to separate, identify, and quantitate specific targeted organic compounds.

3.1.8 *per- and polyfluoroalkyl substances (PFAS), n*—a group of manufactured chemicals consisting of polymeric chains of carbon bonded to fluorine atoms, usually with a polar functional group at the head.

3.1.8.1 *Discussion*—PFAS are fluorinated substances with a carbon chain structure. In perfluoroalkyl substances (PFAAs), each carbon atom in the chain is fully saturated with fluorine

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

PFAS Roadmap: Outline

- Should we design a project to validate ACB Method B21-02?

- And what do I do if I find PFAS?

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