

Oklahoma Department of Environmental Quality
Protocols for PFAS Sampling
Standard Operating Procedures

Air Sampling SOP

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Table:

DEQ PFAS Sampling Quick Reference Field Guide

1.0 General

The objective of this protocol is to give general guidelines for the collection of air samples for PFAS analysis. PFAS air emissions are not regulated under the Clean Air Act (CAA), federal law, or Oklahoma law, and no quantity limits or monitoring requirements are currently applicable to air emissions sources. However, companies and individuals may choose to sample for PFAS in ambient air or stacks. This guidance is based on the DEQ's research and USEPA methods TO-13A, TO-15, SW846 Method 0010, and other test methods (OTM-45). The PFAS General Sampling Guidance should be referred to for what to include in a QAPP for PFAS sampling, information on cross-contamination, additional information on field clothing, and many other details.

2.0 Field Clothing and PPE

Field clothing and other personal protective equipment (PPE) may consist of PFAS-containing materials, especially those advertised as water-resistant, water repellent, or stain-resistant. Refer to Tables 1-4 and 8 in the Quick Reference Field Guide below for general guidance regarding field clothing and PPE.

Sunscreen and biological protection also require screening, and recommendations are provided in Tables 5 and 7 in the Quick Reference Field Guide. For guidance on specific brands and product names, refer to Table 6 in the Quick Reference Field Guide.

While PFAS-containing apparel and PPE should be avoided, the safety of samplers should never be compromised. Any deviation from the DEQ's guidance should be recorded in the field notes.

3.0 Equipment

All equipment used during sample collection should be assessed for the presence of PFAS to eliminate or reduce the probability of cross-contamination. Refer to Table 10 in the Quick Reference Guide at the end of this document for details on sampling containers that are and are not allowed. For air sampling, complex equipment with varying types of components will be used. Equipment specifications can be found in each respective USEPA method document. For methods not designed specifically for PFAS testing (SW846 method 0010, TO-15, and TO-13A), any reasonable modifications to replace equipment containing PFAS (ex- Teflon tubing) with equipment that functions equally but does not contain PFAS should be used. The use of any equipment containing PFAS must be recorded and considered in laboratory findings. Refer to Table 11 in the Quick Reference Field Guide at the end of this document for a list of common materials which are allowed or prohibited. Food packaging can contain PFAS, so food packaging and products should be kept in a designated eating area as noted in Table 9 of the Quick Reference Guide at the end of this document.

4.0 Sampling Techniques and Collection Methods

The following section provides guidance for air sample collection for PFAS analysis. DEQ approves multiple air sampling techniques. The selected sampling technique may vary depending on what is most suitable for the sampling entity, selected laboratory, site characterization, and release type. For air sampling, the kind of air sample (ambient or stack) and the kind of PFAS being assessed will typically determine which sampling equipment and methods are the most suitable. The four possible sampling methods include TO-13A, SW846 Method 0010, SW846 Method 0010 with OTM-45 Modifications, and TO-15. Each of these methods are acceptable for PFAS air analysis. Sample preparations should be outlined in a site-specific sampling plan, such as a Sampling Analysis Plan (SAP). ***Minimal guidance for the setup of these methods is given due to their complexity and specificity. Only experienced air samplers should sample air for PFAS. Please reference the selected USEPA method documents for details pertaining to the implementation of a sampling event.***

PFAS in ambient air can be measured using active (with actual flow) and passive (gas diffusion) sampling techniques. The majority of the available techniques use solid sorbents such as PUF, XAD-2, and sorbent-impregnated PUF (SIP). Active samplers will also include a particulate filter (glass or quartz fiber) ahead of the sorbent module. To optimize detection limits, high-volume air samples are typically used. In the absence of USEPA Federal Reference Methods (FRM) or Toxic Organic Methods (TO) series to measure PFAS compounds in ambient air, modified methods have been developed.

4.1 TO-13A

The DEQ recommends the modified method, TO-13A, for ambient air samples.

Sampling Equipment: This active sampling method utilizes high-volume samplers that contain both a particulate filter and a glass/quartz fiber filter as well as a sorbent cartridge to collect the gaseous and particulate phases.

- Collection should occur at a flow rate of approximately 225 liters/minute, resulting in an air volume greater than 300 m³.
- The solid sorbent used for this method should consist of a “sandwich” of polyurethane foam (PUF) and XAD-2 (polymer of styrene divinylbenzene).

4.2 TO-15

A few PFAS are volatile; for detecting these, the DEQ recommends a modified USEPA Method TO-15.

Sampling Equipment: The atmosphere is sampled by the introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use a pre-evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers.

Pressurized sampling requires an additional pump to provide positive pressure to the sample canister.

- This method is recommended if testing specifically for volatile PFAS compounds. In general, most PFAS are far less volatile than other contaminants. However, a few kinds of PFAS are volatile such as the fluorotelomer alcohols (FTOH).
- A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

4.3 SW846 Method 0010

In the absence of standardized national guidelines for stack testing, sampling and analysis for air stacks have typically been performed using modifications of existing USEPA methods. For semivolatile or nonvolatile PFAS Compounds, the DEQ recommends the following method USEPA 0010 under SW846 (a modified method 5 sampling train) with the further modifications specified by the OTM-45 USEPA method.

Sampling Equipment: The key components of the sampling train include a high-efficiency glass-fiber or quartz-fiber filter and a packed bed of porous polymeric adsorbent resin. The filter collects organic-laden particulate materials and the porous polymeric resin to adsorb semivolatile organic species.

- This method is designed to measure semivolatile organic compounds (compounds with boiling points $>100^{\circ}\text{C}$).
- Particulate and gaseous pollutants should be withdrawn from a stack at an isokinetic sampling rate and be collected in a multicomponent sampling train.

4.4 SW846 Method 0010, OTM-45 Adaptations:

In 2021, the USEPA released OTM-45, which is predominately based on SW846 method 0010. The OTM (other test methods) published by the USEPA have not yet been subject to the federal rulemaking process; thus, OTM-45 currently lacks regulatory approval and is not officially endorsed by the USEPA. The OTM-45 USEPA method is for measuring PFAS air emissions from stationary sources. Currently, OTM-45 can test for 50 specific PFAS compounds and can help improve emissions characterizations. If possible, the OTM-45 guidance, which modifies the SW846 method 0010 for PFAS-specific sampling, should be used. However, if equipment and laboratories which can accommodate the OTM-45 specifications are not available, samplers should resort to the sampling train setup/extraction/analysis methods specified in SW846 method 0010.

- OTM-45 uses a condenser and XAD-2 adsorbent module for the primary capture of PFAS compounds that pass through the glass-fiber or quartz-fiber filter in the gas phase.

- A series of impingers for additional capture of PFAS compounds that pass through the primary XAD-2 adsorbent module are used in OTM-45.
 - A secondary XAD-2 adsorbent module is used to determine the breakthrough of PFAS compounds not captured by the primary XAD-2 adsorbent module and impingers in OTM-45.
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If further information regarding each sampling technique is desired before sampling, please reference the respective USEPA method documents mentioned.

5.0 Decontamination

Refer to Table 13 in the Quick Reference Field Guide at the end of this document for guidance on decontamination methods and materials which are allowed or prohibited while sampling. The following general decontamination principles for PFAS sampling should be followed:

- Sampling equipment must be decontaminated after sampling at each location or at the end of the workday.
- Wash hands with PFAS-free water and don new nitrile gloves before decontamination.
- Decontaminate equipment with a triple rinse of verified PFAS-free water and remove particulates with a polyethylene or PVC brush.
- PFAS-free detergents such as Alconox®, Liquinox®, or Citranox® may be used.
- Dry equipment with a cotton cloth, untreated paper towels, or place decontaminated equipment on a PFAS-free surface to air-dry.

6.0 Quality Assurance / Quality Control

The DEQ recommends following the Quality Assurance/Quality Control (QA/QC) Guidelines outlined in section 5.0 of the General PFAS Sampling document to ensure project-specific Quality Assurance Project Plan (QAPP), Standard Operating Procedures (SOP), and Sampling Analysis Plan (SAP) consistency between sampling events. Additionally, the following guidelines should be followed for air-specific sampling events.

- Duplicate samples should be collected at the rate of 1 per 10 samples.
- Field blanks should be collected if using OTM-45, SW846 Method 0010, or TO-13A. Field blanks should be collected at the rate of one field blank for sampling team per day. Field blanks include the sample bottles containing aliquots of sample recovery solvents, unused filters, and resin cartridges. At a minimum, one

complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The filter housing and probe of the blank train will be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train. (Required)

- Field Sampling Media Blanks (FSMB), also called the field trip blank, should be collected if using OTM-45. FSMB/trip blank, should be collected at the frequency of one per cooler – shipping container. The FSMB is intended to include and represent the sampling media (i.e., filter, XAD-2 adsorbent) and reagents (i.e., impinger contents, rinsing solvents) associated with the field sample collection and recovery but is not used in the field. (Required)
- Sample Train Proof Blanks (STPB) should be collected if using OTM-45. A sample train proof blank train consists of a fully assembled train at the sampling site using glassware that has been cleaned but not yet used for sampling. (Required)
- Sample Train Field Blanks (STFB) should be collected if using OTM-45. Field blanks should be collected at the rate of one field blank per sampling group per day. A sample train field blank train consists of a fully assembled train at the sampling site using glassware that has been previously used for sampling. (Required).
- Pre-sampling Standard Recoveries should be collected if using OTM-45. Pre-sampling standard XAD-2 adsorbent spike recoveries must demonstrate on a per-sample basis that recovery of the labeled standards achieves the requirements in Table 45-5 in USEPA method OTM-45. (Required)
- Secondary XAD-2 Breakthrough determinations should be collected if using OTM-45. These will determine the relative breakthrough of PFAS through the OTM-45 train. For each PFAS target compound, breakthrough should be calculated. (Required)

**These guidelines are not fully comprehensive; the respective USEPA method which will be used should also be referenced for determining quality assurance protocols.*

7.0 Documentation

Keep a sampling log during the sampling event. In the sample log, record the following:

- Sample point location
- Sampling equipment
- Duplicate sample(s)
- Visual description of samples
- Use of any unapproved PPE

- Sample-specific identifiers such as filter numbers with dates and start/end times of sample collection
- All sampling equipment should be assigned identifiers and recorded to differentiate between devices that may be interchanged during prep or certifications
- Other sampling specific (applicable) observations**

** Any sample-specific identifiers such as filter numbers should be recorded in the field notes alongside dates and sample start/end times for later reference. All sampling equipment should also be assigned identifiers and recorded in the field notes to differentiate between devices that may be interchanged during prep or certifications.

Ensure documentation materials are PFAS-free; refer to Table 12 in the Quick Reference Field Guide below. Pre-printed labels for sample containers are preferred.

8.0 Shipment

The following is recommended for sample shipment. Information is also provided in the Quick Reference Field Guide Table 14 at the end of this document.

- Use regular ice, double-bagged, in place of chemical (blue) ice and maintain temperature between +4°C and - 2°C in a cooler.
- Check the cooler periodically to ensure samples are well iced and at the proper temperature.
- The cooler should be taped closed with a custody seal.
- Double bag Chain of Custody and other applicable forms and tape to the inside of the cooler lid.
- Ship within 48 hours or per the holding time determined by the laboratory or the selected laboratory analysis method.

DEQ PFAS Sampling Quick Reference Field Guide

Table 1: Clothing ¹		
Allowed	Not Allowed	Needs Additional Research
<ul style="list-style-type: none"> • Well laundered clothing (recommended six times prior to sampling) • 100% cotton (preferred) • Synthetic fabrics • Polyvinyl Chloride (PVC) • Polyurethane • Uncoated Tyvek® clothing • Wax-coated fabrics. • Rubber/Neoprene 	<ul style="list-style-type: none"> • New/unwashed clothing • Clothing applied/washed with fabric softeners, fabric protectors including ultraviolet (UV) protection, water, dirt or stain-resistant chemicals, or insect-resistant chemicals • Clothing containing Tyvek® • Flame resistant (FR) clothing • Clothing made of Gore-Tex or other known PFAS containing materials. 	<ul style="list-style-type: none"> • Tyvek® suits, clothing that contains Tyvek®, or coated Tyvek®

¹Clothing should be kept dust and fiber free.

Table 2: Boots		
Allowed	Not Allowed	Needs Additional Research
<ul style="list-style-type: none"> • Polyurethane boots • PVC boots • PFAS-free boot covers 	<ul style="list-style-type: none"> • Gore-Tex® boots • Boots made from water-resistant synthetics 	

Table 3: Gloves		
Allowed	Not Allowed	Needs Additional Research
<ul style="list-style-type: none"> • Powderless nitrile gloves* 	<ul style="list-style-type: none"> • Gore-Tex gloves • Any glove made with PFAS-containing materials. 	<ul style="list-style-type: none"> • Latex gloves • Water and dirt-resistant leather gloves • Any special gloves required by a Health and Safety Plan (HASP).

*Samplers must wash their hands with PFAS-free water before putting on any gloves.

Table 4: PPE ¹		
Allowed	Not Allowed	Needs Additional Research
<ul style="list-style-type: none"> • Hard hats made of HDPE • Hard hat covers/liners (i.e. Head Gaiters) made of cotton or other natural fabric • Safety glasses made of HDPE • Life jackets made of polyethylene foam and nylon shell fabric • Waders made of Neoprene or other PFAS-free material 	<ul style="list-style-type: none"> • Waders made of Gore-Tex or other known PFAS containing materials 	<ul style="list-style-type: none"> • Hard hats or safety glasses not made of HDPE

¹PPE should be kept dust and fiber free.

Table 5: Sun Protection		
Allowed	Not Allowed	Needs Additional Research
• Approved Sunscreens (See Table 6)	• No unauthorized sunscreen	

Table 6: Allowed/Approved Sunscreens ¹
• Banana Boat® for Men Triple Defense Continuous Spray Sunscreen SPF 30
• Banana Boat® Sport Performance Coolzone Broad Spectrum SPF 30
• Banana Boat® Sport Performance Sunscreen Lotion Broad Spectrum SPF 30
• Banana Boat® Sport Performance Sunscreen Stick SPF 50
• Coppertone® Sunscreen Lotion Ultra Guard Broad Spectrum SPF 50
• Coppertone® Sport High-Performance AccuSpray Sunscreen SPF 30
• Coppertone® Sunscreen Stick Kids SPF 55
• L'Oréal® Silky Sheer Face Lotion 50
• Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 50
• Meijer® Sunscreen Continuous Spray Broad Spectrum SPF 30
• Meijer® Clear Zinc Sunscreen Lotion Broad Spectrum SPF 15, 30 and 50
• Meijer® Wet Skin Kids Sunscreen Continuous Spray Broad Spectrum SPF 70
• Neutrogena® Beach Defense Water+Sun Barrier Lotion SPF 70
• Neutrogena® Beach Defense Water+Sun Barrier Spray Broad Spectrum SPF 30
• Neutrogena® Pure & Free Baby Sunscreen Broad Spectrum SPF 60+
• Neutrogena® UltraSheer Dry-Touch Sunscreen Broad Spectrum SPF 30

¹Baby sunscreens that are “free” or “natural” are not guaranteed PFAS-free and need additional research.

Table 7: Insect Protection¹

Allowed	Not Allowed	Needs Additional Research
<ul style="list-style-type: none"> • OFF® Deep Woods • Sawyer® Permethrin 	<ul style="list-style-type: none"> • No unauthorized insect protection 	

¹Approved sunscreens and insect repellents should not be applied near the sample collection area. Hands should be well washed after application or handling of these products, and afterwards; an uncontaminated clean/new pair of powderless nitrile gloves should be worn.

Table 8: Prohibited Water Repellant Field Clothing and PPE Brand and Product Names

• Ultra Release Teflon®	• Release Teflon®
• Repel Teflon® Fabric Protector	• High-Performance Release Teflon®
• High-Performance Repel Teflon® Fabric Protector	• Advanced Dual Action Teflon® Fabric Protector
• NK Guard® S Series	• GreenShield®
• Tri-Effects Teflon® Fabric Protector	• Lurotex Protector RL ECO®
• Oleophobol CP®	• Repellan KFC®
• Rucostar® EEE6	• Unidyne™
• Bionic Finish®	• RUCO-GUARD®
• RUCOSTAR®	• RUCO-COAT®
• RUCO-PROTECT®	• RUCOTEC®
• RUCO®	• Resist Spills™
• Resists Spills and Releases Stains™	• Scotchgard™ Fabric Protector
• GoreTex®	

Table 9: Food Containers

Allowed	Not Allowed	Needs Additional Research
• Food packaging and products in a designated eating area set up for food and beverage consumption	• Food packaging and products in the staging or sampling areas	• Bringing foods rewrapped in PFAS-free materials

Table 10: Sampling Containers		
Allowed	Not Allowed	Needs Additional Research
<ul style="list-style-type: none"> • HDPE also known as polyethylene high-density (PEHD) • Polypropylene • Stainless Steel • Unlined bottle caps • LDPE resealable bags (Ziplock) that will not come in contact with the sample media 	<ul style="list-style-type: none"> • Polytetrafluoroethylene (PTFE) lined bottles or caps (i.e. Teflon® and Hostaflo®) • LDPE containers that will contact the sample media • Aluminum foil is not to be used due to the possibility of it being coated with PFAS. Utilize an alternative sample preparation and storage material. 	<ul style="list-style-type: none"> • Glass bottles and containers¹

¹Glass bottles or containers may be used if they are known to be PFAS-free; however, PFAS have been found to adsorb to glass, especially when the sample is in contact with the glass for an extended period of time (e.g., stored in a glass container). If the sample comes into direct contact with the glass for a short period of time (e.g., using a glass container to collect the sample, then transferring the sample to a non-glass sample bottle), the adsorption is minimal. Generally, glass bottles or containers should not be used for PFAS samples.

Table 11: Sampling Equipment		
Allowed	Not Allowed	Needs Additional Research
<ul style="list-style-type: none"> • HDPE (also PEHD) • Polypropylene • Stainless Steel • Acetate • Silicone 	<ul style="list-style-type: none"> • Polytetrafluoroethylene (PTFE) • Polyvinylidene fluoride (PVDF) • Polychlorotrifluoroethylene (PCTFE) • Ethylene-tetrafluoroethylene (ETFE) • Low-density polyethylene (LDPE) which will contact the sample media 	<ul style="list-style-type: none"> • Glass equipment

Table 12: Field Materials		
Allowed	Not Allowed	Needs Additional Research
<ul style="list-style-type: none"> • Aluminum, polypropylene, or Masonite field clipboards • Rite in the Rain® notebooks • Loose paper (non-waterproof, non-recycled) • Ballpoint pens and pencils 	<ul style="list-style-type: none"> • Clipboards coated with PFAS-containing materials • Notebooks made with PFAS treated paper • PFAS treated loose paper • Post-It® Notes or other adhesive paper products • Sharpie® markers • Coated materials, including paper towels • Aluminum foil is not to be used due to the possibility of it being coated with PFAS. Utilize an alternative preparation and storage material. 	<ul style="list-style-type: none"> • Plastic clipboards, binders, or spiral hardcover notebooks • Waterproof field books • All markers not listed as allowable

Table 13: Decontamination Procedures

Allowed	Not Allowed	Needs Additional Research
<ul style="list-style-type: none"> Alconox®, Liquinox®, or Citranox® Triple rinse with PFAS-free water Cotton cloth or untreated paper towels Polyethylene or PVC brush to remove particulates 	<ul style="list-style-type: none"> Decon 90® PFAS treated paper towels Reusing non-dedicated equipment without decontaminating 	<ul style="list-style-type: none"> Municipal water¹ Recycled or treated paper towels

¹Decontamination procedures should include a triple rinsing with PFAS-free water for equipment such as dippers, balers, spades, etc. Laboratory supplied PFAS-free deionized water is preferred for cleaning and decontamination. However, commercially available deionized water may be used for cleaning and decontamination if the water is verified to be PFAS-free. Municipal drinking water may be used for cleaning or decontamination if the water is known to be PFAS-free.

Table 14: Sample Shipment

Allowed/Required	Not Allowed	Needs Additional Research
<ul style="list-style-type: none"> Coolers filled with regular ice Maintaining sample temperature between +4°C and -2°C Double-bagging of samples and ice using bag materials made of HDPE (preferred) or LDPE (if sample does not come in contact) Chain of Custody and other forms should be single bagged in LDPE (e.g. Ziploc®) storage bags and taped to the inside of the cooler lid. 	<ul style="list-style-type: none"> Aluminum foil is not to be used due to the possibility of it being coated with PFAS. Utilize an alternative sample preparation and storage material. Chemical (blue) ice packs 	<ul style="list-style-type: none"> Chemical (blue) ice packs that are verified PFAS free