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SOP for Extraction of Fluorinated Residuals

This document captures protocols for extraction of residual compounds for the purpose of targeted PFAS quantitation. **The resulting extracted solutions can be analyzed by a certified lab using appropriate methods (e.g. ISO 21675 Method).** This applies to extracts from matrices described below **except** Indirect Precursors (IDPs) and Telomer Intermediates, where residuals are measured by gas chromatography with triple quadrupole detection (GC/QqQ).

Equipment:

- Cryogrinder (SPEX SamplePrep 6875 Freezer/Mill, or equivalent)
- Heated Sonicator (Branson CPX2800H, or equivalent)
- Centrifuge (Eppendorf 5430 Microcentrifuge with F-35-6-30 Rotor, or equivalent)
- Balance capable of measurement to four decimal places
- Digital thermometer
- Vortex mixer
- Wrist action shaker

Consumables / Solvents:

Please note: Avoid using glass or PTFE containing materials. All consumables should be HDPE or PP materials.

- 50 mL free-standing centrifuge tubes
- 15 mL centrifuge tubes
- 4 mL Cryo storage vials
- Transfer pipets
- LC/MS grade methanol
- LC/MS grade ethanol
- Vertrel™ XF
- Liquid nitrogen
- Milli-Q water
- Ottawa Sand
- Ammonium Hydroxide (NH_4OH)
- Potassium Hydroxide (KOH)
- GC and LC vials
- Headspace GC vials

Extraction Procedure:

Solid Polymer Resins :

1. Grind approximately 9 g polymer resin in duplicate tubes using cryogrinder with liquid nitrogen (3 cycles, 10 min each, rate: 15). A visual inspection of the cryoground product must be performed; an acceptable product has homogenous particle size with the consistency of a fine powder. If the sample is not fully ground, repeat cyrogrinding until desired consistency has been achieved.
2. Weigh approximately 8 g of cryoground sample into a tared 50 mL centrifuge tube; record weight. Weigh a second 8 g aliquot to prepare a duplicate sample.
3. Add 25 mL of LC/MS grade methanol into each duplicate tube.
4. Sonicate tubes in a 60 ^oC water bath for 6 hours.
5. After sonication, remove centrifuge tubes and allow to cool to room temperature.
6. Centrifuge tubes for 15 minutes at 6000 rpm.
7. Transfer 15 mL of the methanol extract into a clean 15 mL centrifuge tube.
8. To the original 50 mL sample tubes, add a fresh 15 mL aliquot of methanol. Vortex samples for 30 seconds to break up packed polymer.
9. Repeat Steps 4 through 8 for a total of three sequential extractions per sample.

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10. From each tube of extracted sample (6 vials total per sample), transfer approximately 2 mL to a labeled cryovial to be stored as retains.

Granular and Fine Powder Polymer :

1. **Granular and Fine Powder Polymer:** Polymer samples received in a granular or fine powder form do not need to be cryoground. Follow the extraction protocol (Solid Polymer Resins) starting from Step 2.

Fluoroelastomers (FKM):

Please note: Certain FKM grades will dissolve / swell in methanol. Sample grades with unknown stability in methanol should be tested to make sure no dissolution / swelling is observed. Recommended procedure is putting 2 g of polymer in 15 mL of methanol for 6 hours at 60 °C under sonication. At the end of this test if the polymer is no longer observed to be discrete cubes this FKM extraction procedure should be followed but the extraction solvent should be ethanol.

1. Fluoroelastomer (FKM) samples received in crumb form do not need to be cryoground or chopped. Follow the extraction protocol (Solid Polymer Resins) starting from Step 2. For FKM in sheets, samples should be chopped into fine pieces (~2 x 2 mm) with scissors to maximize surface area for extraction. Cured FKM, i.e. crosslinked material, should be cryoground following the extraction protocol (Solid Polymer Resins) starting from Step 1.

Polymer Films:

1. Polymer samples received in film form should be chopped into fine pieces (~2 x 2 mm) with scissors to maximize surface area for extraction. Follow the extraction protocol (Solid Polymer Resins) starting from Step 2. *Please note: ensure the sample is below the solvent line prior to extraction.*

Calcium Fluoride (CaF_2) :

1. Samples do not require cryogrinding. CaF_2 is extracted using 5 g of CaF_2 in 10 mL of 0.4 wt. % KOH in methanol for 3 hours under sample agitation, where 0.4 wt. % KOH in methanol is recommended to keep the extraction basic and prevent formation of HF. Extract at elevated temperature is recommended to improve extraction efficiency.

Polymer Dispersions

1. Weigh approximately 5 g of dispersion into a tared 50 mL centrifuge tube; record weight. Weigh a second 5 g aliquot to prepare a duplicate sample.
   Please note: sample should be mixed to homogenize the dispersion prior to sampling.
2. Add 20 mL of 0.4 wt. % KOH in methanol into each duplicate tube.
3. Vortex tubes for 30 minutes.
4. Sonicate tubes in a 60 °C water bath for at least 12 hours.
5. After sonication, remove centrifuge tubes and allow to cool to room temperature.
6. Vortex tubes for 30 seconds to redistribute the solids in the dispersion.
7. Centrifuge tubes for 15 minutes at 6000 rpm.
8. Transfer 15 mL of the methanol extract into a clean 15 mL centrifuge tube.
9. From each tube of extracted sample (2 vials total per sample), transfer approximately 2 mL to a labeled cryovial to be stored as retains.

Lubes and Greases:

1. Weigh approximately 4 g of sample into a tared 50 mL centrifuge tube; record weight. Weigh a second 4 g aliquot to prepare a duplicate sample.
2. Add 48 g of Vertrel XF into each duplicate tube; record weight.
3. Vortex samples for 30 seconds.
4. Add 8 mL of 1 wt. % NH_4OH in methanol:water / 50:50 (v:v) to each duplicate tube.
5. Place tubes on wrist action shaker for 5 minutes or shake vigorously by hand.

6. Centrifuge the tubes at 6000 rpm for 20 minutes. After centrifugation 2 phases will appear. The top phase is the methanol:water phase.
7. Using a transfer pipette, aliquot approximately 5 mL of the methanol:water phase into a clean 15 mL tube.
8. To the original 50 mL sample tubes, add an additional 8 mL of 1 wt. % NH_4OH in methanol:water / 50:50 (v:v).
9. Repeat Steps 4 through 8 for a total of three sequential extractions per sample.
10. From each tube of extracted sample (6 vials total per sample), transfer approximately 2 mL to a labeled cryovial to be stored as retains.

IXM Membranes:

Please note: IXM membranes are observed to swell in the presence of typical organic solvents limiting solvent recovery. A method of preswelling the membrane before extraction is used to first swell the membrane and then extract to maximize solvent recovery.

1. The IXM membrane should be chopped into fine pieces (~2 x 2 mm) with scissors to maximize surface area for extraction.
2. Weigh approximately 4 g of sample into a tared 50 mL centrifuge tube; record weight. Weigh a second 4 g aliquot to prepare a duplicate sample.
3. Add 11 g of Milli-Q water into each duplicate tube; record the weight.
4. Vortex tubes for 5 minutes.
5. Centrifuge tubes for 5 minutes at 6000 rpm.
6. Add 11 g of methanol into each duplicate tube; record the weight.
7. Vortex the tube again for 5 minutes.
8. Centrifuge tubes for 5 minutes at 6000 rpm to compact the membrane at or below the solvent level prior to extraction.
9. Sonicate tubes in a 60 ^{o}C water bath for 6 hours.
10. After sonication, remove centrifuge tubes and allow to cool to room temperature.
11. Centrifuge tubes for 15 minutes at 6000 rpm.
12. Using a transfer pipette, aliquot the methanol:water phase into a clean 15 mL tube without any transfer of membrane. Record the weight of the solvent removed.
13. To the original 50 mL sample tube, add back the weight of solvent removed in step 12 by:
    1. Adding water equaling 50 % of the total weight removed in Step 12.
    2. Vortexing tubes for 5 minutes.
    3. Centrifuging tubes for 5 minutes at 6000 rpm.
    4. Adding methanol equaling 50 % of the total weight removed in Step 12.
    5. Vortexing tubes for 5 minutes.
    6. Centrifuging tubes for 5 minutes at 6000 rpm.

    Example: If 14 g of solvent was removed, 7 g of water and 7 g of methanol should be added back following the procedure above.
14. Sonicate tubes in a 60 ^{o}C water bath for 6 hours.
15. After sonication, remove centrifuge tubes and allow to cool to room temperature.
16. Centrifuge tubes for 15 minutes at 6000 rpm.
17. Using a transfer pipette, aliquot the methanol:water phase into a clean 15 mL tube without any transfer of membrane. Record the weight of the solvent removed.
18. To the original 50 mL sample tube, add back the weight of solvent removed in step 17 by:
    1. Adding water equaling 50 % of the total weight removed in Step 17.
    2. Vortexing tubes for 5 minutes.
    3. Centrifuging tubes for 5 minutes at 6000 rpm.
    4. Adding methanol equaling 50 % of the total weight removed in Step 17.
    5. Vortexing tubes for 5 minutes.
    6. Centrifuging tubes for 5 minutes at 6000 rpm.

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19. From each tube of extracted sample (6 vials total per sample), transfer approximately 2 mL to a labeled cryovial to be stored as retains.

Indirect Precursors and Residual Telomer Intermediates Analyses

Please note: The targeted precursors in intermediates are measured through a gas chromatographic separation followed by detection by tandem mass spectrometry triple quadruple detection operating in the MRM mode (GC/QqQ) via chemical ionization.

1. Samples must be shaken well prior to sampling.
2. Accurately weigh 0.020 ± 0.002 g of sample into a GC vial, then record the weight of sample.
3. Add Vertrel™ XF to the vial and then record the total weight. The total weight should be 1.00 ± 0.02 g.

PFOA in Fluorotelomers by Headspace GC/MS

Please note: Analysis of perfluorooctanoic acid (PFOA) is performed with a headspace GC sampling method. Compounds are derivatized to the methyl ester using methanolic sulfuric acid and heated. The headspace of the heated vial is injected and analytes quantified via gas chromatography tandem mass spectrometry triple quadrupole detection (GC/QqQ) operating in MRM mode using both electronic (EI) and chemical (CI) ionization.

1. Prepare a methylation Reagent Solution of methanol and sulfuric acid (cc) with ratio of 80:20 (v:v)
2. Weigh 0.04 g (~26.7 µL) of sample into a headspace GC vial and record the weight.
3. Add 960 µL of deionized or MilliQ water and record the total weight of sample plus water weight.
4. Add 3 mL methylation solution into a headspace vial and then crimp the vial cap
5. Vortex sample for 5 seconds.

Telomer Intermediates for Fluorinated Residuals: Organic Acids

1. Using an analytical balance, add 4 grams of H_2O to a 20 mL scintillation vial.
2. Add 1 g of telomer intermediate to the same vial.
3. Shake vigorously for 0.5 – 1 minute.
4. Let the solution settle for 4 hours to phase separate. Note: The aqueous extract is the top layer.
5. Remove 400 µL of the aqueous extract and transfer to a LC vial while avoiding drawing up any intermediate in the lower layer.
6. Add 400 µL of MeOH to the LC vial. Cap and crimp the vial. Invert the vial several times to mix.

Recommended Quality Assurance

Blanks:

1. A method blank should be prepared and submitted for testing along with extracted samples.
2. For each set of extractions of *cryoground* polymer, an equipment blank should be collected by cryogrinding and extracting Ottawa sand and analyzing with the extracted samples.

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Calculations for Final Concentration with Respect to the Initial Polymer Extract in ppbw (ng/g)

Solid Polymer Resins, Granular or Fine Powder Polymer, Fluoroelastomers (FKM), Polymer Films:

$$\text{Sample Result } \left(\frac{\text{ng}}{\text{g}}\right) = \frac{\text{Sum Total of Concentration in Extract (ng/mL) * Average Extraction Volume (mL)}}{\text{Sample Weight (g)}}$$

Sum Total of Conc. in Extract (ng/mL) = Extract Conc. Measured in Extraction 1 (ng/mL) + Extract Conc. Measured in Extraction 2 (ng/mL) + Extract Conc. Measured in Extraction 3 (ng/mL)

$$\text{Average Extraction Vol. (mL)} = \frac{\text{Vol. Extraction Solvent 1 (mL) + Vol. Extraction Solvent 2 (mL) + Vol. Extraction Solvent 3 (mL)}}{3}$$

Polymer Dispersions:

$$\text{Sample Result } \left(\frac{\text{ng}}{\text{g}}\right) = \frac{\text{Sum Total of Concentration in Extract (ng/mL) * Total Extraction Volume (mL)}}{\text{Sample Weight (g)}}$$

Total extraction volume (mL) = volume of H_2O in sample (mL) + 20 mL of 0.4% KOH Methanol added (mL)

Lubes and Greases:

$$\text{Sample Result } \left(\frac{\text{ng}}{\text{g}}\right) = \frac{\text{Sum Total of Concentration in Extract (ng/mL) * Average Extraction Volume (mL)}}{\text{Sample Weight (g)}}$$

Sum Total of Conc. in Extract (ng/mL) = Extract Conc. Measured in Extraction 1 (ng/mL) + Extract Conc. Measured in Extraction 2 (ng/mL) + Extract Conc. Measured in Extraction 3 (ng/mL)

$$\text{Average Extraction Vol. (mL)} = \frac{\text{Vol. Extraction Solvent 1 (mL) + Vol. Extraction Solvent 2 (mL) + Vol. Extraction Solvent 3 (mL)}}{3}$$

IXM Membranes:

$$\text{Sample Result } \left(\frac{\text{ng}}{\text{g}}\right) = \frac{\text{Sum Total of Concentration in Extract (ng/mL) * Average Extraction Volume (mL)}}{\text{Sample Weight (g)}}$$

Sum Total of Conc. in Extract (ng/mL) = Extract Conc. Measured in Extraction 1 (ng/mL) + Extract Conc. Measured in Extraction 2 (ng/mL) + Extract Conc. Measured in Extraction 3 (ng/mL)

$$\text{Average Extraction Vol. (mL)} = \frac{\text{Vol. Extraction Solvent 1 (mL) + Vol. Extraction Solvent 2 (mL) + Vol. Extraction Solvent 3 (mL)}}{3}$$

$$\text{Extraction Volume 1 (mL)} = \frac{\text{Weight Solvent Added Extraction 1 (g)}}{\text{density of extraction solvent (g/mL)}}$$

$$\text{Extraction Volume 2 (mL)} = \frac{\text{Weight Solvent Added Extraction 2 (g)}}{\text{density of extraction solvent (g/mL)}}$$

$$\text{Extraction Volume 3 (mL)} = \frac{\text{Weight Solvent Added Extraction 3 (g)}}{\text{density of extraction solvent (g/mL)}}$$

Please note: if the extraction solvent ratio is kept as methanol:water / 50:50 (w:w) throughout the extraction, the density of extraction solvent will be 0.8955 g/mL.