Determination of the concentration of polar per- and polyfluoroalkyl compounds (PFAS) in a guided gas stream

CONTENT

1 PURPOSE AND SCOPE

This procedure describes a method for the quantitative determination of polar per- and polyfluoroalkyl compounds (PFAS) in a guided gas stream. It includes the concentration determination in mass per unit gas volume (ng/Nm³) of both volatile (<C4) and semi-volatile PFAS via LC-MS/MS analysis of the following samples originating from a sampling train (see schematic representation in Figure 1):

- Rinsing liquids: methanol and cyclohexane
- Filter
- XAD-2: 1 primary and 1 secondary (breakthrough) module
- Water fraction: condensate and impinger water

The procedure is aimed at the quantitative analysis of 28 PFAS compounds that were subject to a validation test based on 4 repeated measurements (+ field blank) with spiked sampling trains during an interlaboratory test (ILC) in February, 2024 (Hofman et al., 2025a). The sampling trains were equipped with media (filter/XAD-2/impinger water) spiked with native PFAS (50 cpds) at representative concentration levels. The associated measurement uncertainty (U, k=2) according to WAC/VI/A/002 and apparent total train recovery for each native compound is shown in Table 1. For quantitative analysis, U <50% and total train recovery of 70- 120% are required for both the sampling (LUC/VI/003) and analysis (WAC/IV/A/025). The LOQs were determined per analytical fraction as 10x the standard deviation based on 5 repeated measurements (n=5) at both low (0.05 ng/fraction) and higher (3 ng/fraction) spiked fractions. The resulting LOQs are provided in Table 1.

Most PFAS compounds only have a linear form. Several branched isomers (same molecular formula, different structural formula) can occur for a number of perfluorinated compounds (PFOA, PFHxS, PFOS, PFOSA, MePFOSA, EtPFOSA, MePFOSAA and EtPFOSAA). In this procedure, L-PFOA, L-PFHxS, L-PFOS, L-PFOSA, L-MePFOSA, LEtPFOSA, L-MePFOSAA and L-EtPFOSAA refer to the linear form. The total concentration (sum of linear and branched compounds) is reported separately as respectively T-PFOA, T-PFHxS, T-PFOS, T-PFOSA, T-MePFOSA, T-EtPFOSA, T-MePFOSAA and T-EtPFOSAA.

Table 1 Measurement uncertainty (U), total spike recovery (%) and limit of quantification (LOQ) of the quantitative PFAS compounds as determined by a validation test. For 8 compounds a distinction is made between the linear form (L-) and the sum of linear and b ranched isomers (T-)

COMPOUND	CAS	REC (%)	U (k=2)	LOQ*		
		%	%	XAD-2	Filter	OW
				ng	ng	ng
PFBA	375-22-4	120%	34%	ND	0.9	0.01
PFPeA	2706-90-3	100%	2%	3	0.8	0.01
PFHxA	307-24-4	98%	10%	1	1.3	0.01
PFHpA	375-85-9	93%	14%	0.9	0.9	0.01
L-PFOA	335-67-1	91%	19%	5	0.1	0.01
PFNA	375-95-1	92%	20%	0.8	0.01	0.01
PFDA	335-76-2	99%	15%	2	0.05	0.01
PFUnDA	2058-94-8	104%	28%	0.2	0.04	0.01
PFDoDA	307-55-1	107%	33%	0.5	0.04	0.01
PFTeDA	376-06-7	96%	50%	0.3	0.01	0.01
PFBS	375-73-5	96%	7%	0.4	0.8	
PFPeS	2706-91-4	91%	13%	0.03	0.03	0.01
L-PFHxS	355-46-4	92%	15%	0.05	0.05	0.01
PFHpS	375-92-8	86%	26%	0.07	0.04	0.01
L-PFOS	1763-23-1	101%	8%	3	0.8	0.01
PFNS	68259-12-1	90%	21%	0.08	0.04	0.01
PFDS	335-77-3	85%	28%	0.1	1.2	0.01
4:2FTS	757124-72-4	98%	3%	0.02	0.4	0.01
6:2FTS	27619-97-2	93%	11%	2.7	0.8	0.01
8:2FTS	39108-34-4	93%	22%	0.1	0.5	0.01
PFBSA	30334-69-1	100%	5%	6	1.8	0.01
MePFBSAA	159381-10-9	103%	5%	0.8	0.1	0.01
PFHxSA	41997-13-1	97%	14%	0.4	0.8	0.01
L-MePFOSAA	2355-31-9	94%	21%	0.05	0.01	0.01
L-EtPFOSAA	2991-50-6	97%	22%	0.05	0.7	0.01
HFPO-DA	13252-13-6	102%	8%	3.5		0.01
DONA	919005-14-4	89%	17%	0.1	0.02	0.01
PFECHS	646-83-3	88%	22%	0.1	0.04	

** The LOQs were determined per analytical fraction as 10x the standard deviation based on 5 repeated measurements (n=5) at both low (0.05 ng/fraction) and higher (3 ng/fraction) spiking levels.*

In addition to the 28 quantitative compounds, 14 compounds can be indicatively quantified (Table 2). During the ILC, these compounds showed a higher measurement uncertainty (>50%), deviating total train recoveries (<70% or >120%), or are listed as indicative in the WAC/IV/A/025.

Table 2 Measurement uncertainty (U), total spike recovery (%) and limit of quantitation (LOQ) of the indicative PFAS components as determined by a validation test. For 8 components a distinction is made between the linear form (L-) and the sum of linear and bra nched isomers (T-).

COMPOUND	CAS	REC (%)	U (k=2)	LOQ		
		%	%	XAD-2	Filter	OW
				ng	ng	ng
PFTrDA	72629-94-8	109%	34%	0.1	0.01	
PFHxDA	67905-19-5	80%	59%	0.5	0.03	0.01
PFODA	16517-11-6	51%	117%	ND	0.7	
PFUnDS	749786-16-1	81%	34%	0.09	0.03	
PFDoDS	79780-39-5	79%	36%	0.03	0.7	
PFTrDS	791563-89-8	72%	51%	0.02	0.02	
10:2FTS	120226-60-0	108%	29%	0.1	0.7	0.05
MePFBSA	68298-12-4	55%	140%	ND	1.4	0.01
L-PFOSA	754-91-6	56%	85%	0.08	0.8	0.01
L-MePFOSA	31506-32-8	1%	273%	0.2	1.4	0.01
L-EtPFOSA	4151-50-2	0%	289%	ND	0.7	0.01
6:2diPAP	57677-95-9	92%	47%	0.09	0.005	
6:2/8:2diPAP	943913-15-3	81%	63%	0.1	0.05	0.05
8:2diPAP	678-41-1	67%	72%	0.7	0.08	0.01

** The LOQs were determined per analytical fraction as 10x the standard deviation based on 5 repeated measurements (n=5) at both low (0.05 ng/fraction) and higher (3 ng/fraction) spiking levels.*

For the semi-volatile (C4-C18) polar PFAS, the analytical coverage will be expanded with additional compounds listed in the most recent WAC/IV/A/025, namely 11 quantitative and 16 optional compounds. Although these compounds are already validated for water (WAC/IV/A/025), the validation for the remaining LUC/VI/003 fractions is still ongoing. Awaiting these validation results, the new WAC/IV/A/025 compounds can already be optionally reported.

For the volatile (<C4) polar PFAS, 7 compounds can be analysed optionally following the WAC/IV/A/026 procedure ({VITO, 2025 #1708}). This method requires a different sampling preparation for the water fraction (§4.5), solvent-ratios in the final extract (§4.2-4.6) and LC-MS/MS configuration (WAC/IV/A/026). In the water fraction, these compounds can be quantified from concentration levels reported in

Table 3 Quantifiable volatile (<C4) polar PFAS according to WAC/IV/A/026

PFAS	CAS	ng/L
TFA	76-05-1	100 – 500
PFPrA	422-64-0	10 – 50
PFPrS	423-41-6	10 – 50
TFMS	1493-13-6	10 – 50
PFEtS	354-88-1	50 – 250
2,3,3,3-TeFPrA	359-49-9	100 – 500
2,2,3,3-TeFPrA	756-09-2	10 – 50

2 PRINCIPLE & SAMPLING SETUP

To monitor polar PFAS in guided emissions, two sampling train variants are allowed, respectively based on flue gas sampling with a heated or cooled probe. The heated sampling train variant is derived from US EPA OTM-45 method (published on 13/1/2021[1] and revised on 14/1/2025[2]) and optimized based on extensive field and lab validations {Hofman, 2025 #1676;Hofman, 2025 #1690}, while the cooled probe variant is derived from the EN 1948-1 sampling train. The equivalence of both sampling train variants was evaluated during an interlaboratory comparison {Hofman, 2024 #1748}.

2.1 HEATED SAMPLING PROBE

Flue gas is sampled isokinetically (same magnitude and direction of gas flow) by means of a heated sampling probe. Particle-bound PFAS are captured on a heated quartz fiber filter (120 °C or at least 10 °C above chimney temperature), after which the flue gas condenses in the condensate flask, semi-volatile PFAS are captured in a series of water-filled impingers and most volatile compounds captured in sequential adsorbent (XAD-2) cartridges.

The heated sampling train configuration is shown in Figure 1 and consists of:

- a heated probe with quartz fiber filter
- a condenser
- an empty condensate flask to capture the condensate
- a series of 2 impingers filled with ultrapure water
- a primary and secondary (breakthrough) adsorbent (XAD-2) cartridge
- a drying tower (silica or equivalent desiccant) with pump

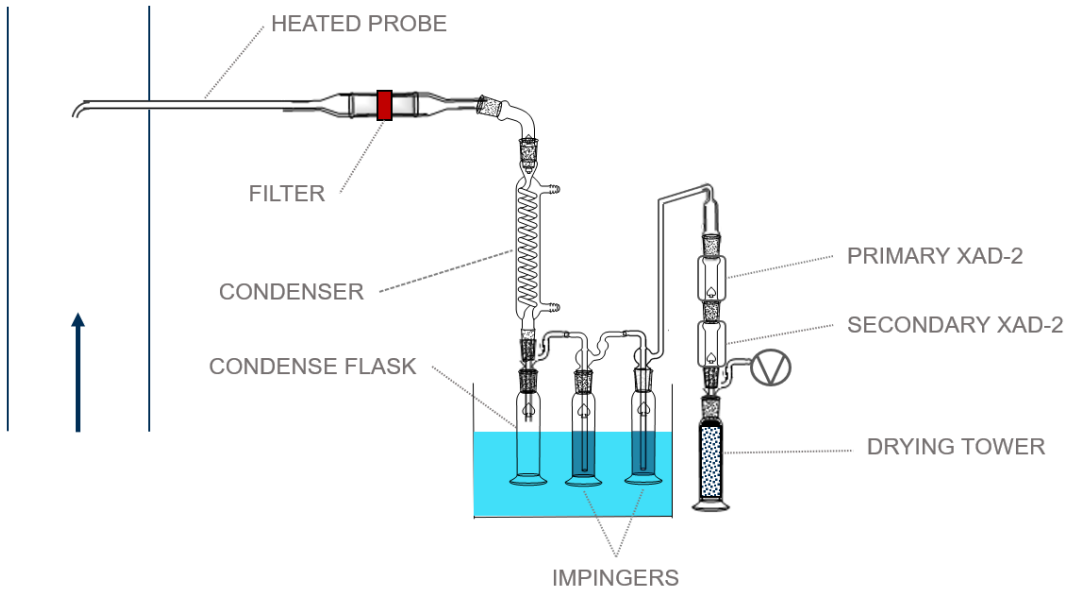


Figure 1 Schematic representation of the heated sampling train variant

[1] https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf
[2] https://www.epa.gov/system/files/documents/2025-01/other-test-method-45-rev1-final-1-14-25.pdf

2.2 COOLED SAMPLING PROBE

Flue gas is sampled isokinetically (same magnitude and direction of gas flow) by means of a cooled sampling probe. The flue gas condenses and is captured together with the potential dust phase in the condensate flask, semi-volatile PFAS are captured in a series of water-filled impingers, remaining particle-bound PFAS captured on glasswool or quartz fiber filter and volatile PFAS captured in sequential adsorbent (XAD-2) cartridges.

The cooled sampling train configuration is shown in Figure 2 and consists of:

- a cooled sampling probe
- an empty condensate flask to capture the condensate
- a series of 2 impingers filled with ultrapure water
- a primary and secondary (breakthrough) adsorbent (XAD-2) cartridge
- a drying tower (silica or equivalent desiccant) with pump

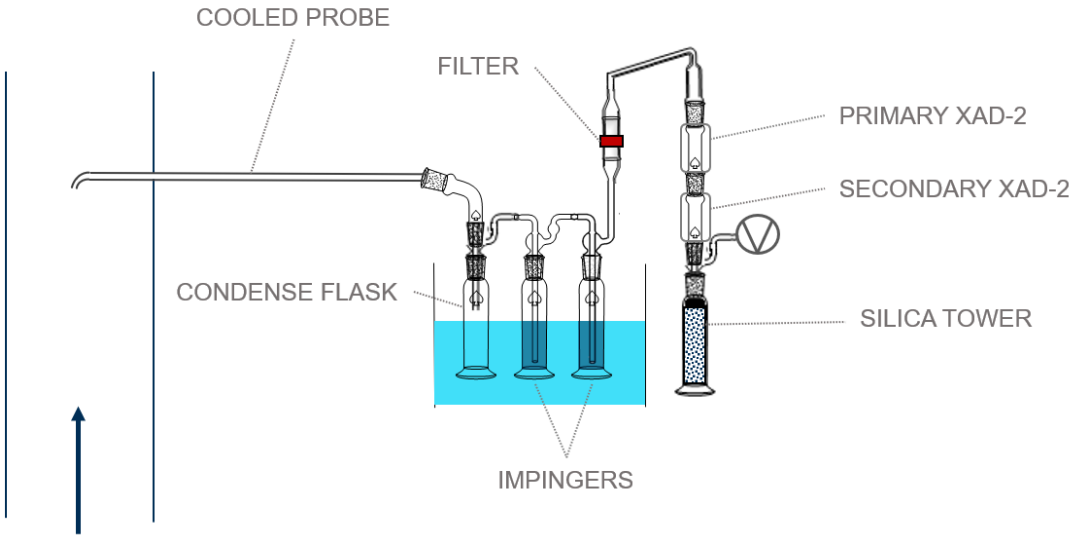


Figure 2 Schematic representation of the cooled sampling train variant

The sampling train consists of borosilicate or quartz glass (probe, filter holder, condenser, condenser bottle, impingers, etc.). Although Teflon (PTFE) should be avoided as much as possible (risk of contamination), it can be used in connection, O-rings and/or coatings provided that the applied material is tested beforehand. Polypropylene (PP), polyethylene (PE, HDPE) or glass can be used to replace PTFE. Any contamination in the applied sampling media (filter, XAD-2, water, rinsing solvents) or sampling train can be identified in the corresponding medium and field blanks.

Further specifications for the different parts of the sampling train include:

- The quartz filter has an efficiency of at least 99.95% (<0.05% penetration) for 0.3 µm particles and is kept at a temperature of 120±12°C (or minimal 10°C above stack temperature) during the chimney measurement to avoid condensation/moisture on the filter. This temperature must be measured in the filter housing.
- Condensate flask and impingers are cooled during the measurement
- Adsorbent cartridges consist of water-jacketed glass cartridges containing 20-40 g of solid adsorbent (XAD-2).

- The temperature of the incoming gas flow at the XAD-2 cartridges must be kept below 20°C. This (incoming) temperature is measured at the primary XAD-2 cartridge. An ice bath can be used to circulate pump-cooled water to the condenser and adsorbent cartridges. If the ambient temperature is >20°C, the XAD-2 cartridges are required to be cooled.
- Impingers are of the standard type.
- The adsorbent (XAD-2) is stored and transported in glass cartridges or clean wide mouth HDPE jars.
- During sampling, the XAD-2 cartridges are wrapped with aluminum foil to protect the adsorbent from radiant heat and sunlight
- The impingers are filled with approximately 100 mL ultra pure water

Recovery of the emission samples takes place in existing cartridges (e.g. XAD-2) or polyethylene (HDPE) recipients and results in 20 samples (S1-S20 in Appendix 1; including medium-, field- and post-rinse blanks) that are subsequently aggregated to 6 analytical fractions .

3 SAMPLING PROCEDURE

3.1 PREPARATION

All glassware must be uniquely marked in advance, so that traceability of contamination is possible. Depending on the (re)use of the glassware, there are 2 different cleaning procedures. The sampling probe liner and filter housing are replaced with each measurement and rinsed with methanol.

The following applies to new glassware:

- The glassware (except probe liner) is rinsed with warm water maximum 2 weeks prior to sampling, then rinsed with methanol and dried at 150°C. Pending sampling, the glassware is stored in a sealed recipient.
- The glass liner of the sampling probe is rinsed with methanol

The following applies to existing glassware that is reused:

- The glassware (except probe liner) is cleaned with warm water maximum 2 weeks prior to sampling and rinsed successively with methanol and cyclohexane.
- After cleaning with methanol and cyclohexane, the glassware is oven dried at minimal 450°C for at least 3 hours. The glassware is now ready for sampling. Pending sampling, the glassware is stored in a sealed recipient.
- Sampling probe liner and filter housing are replaced with each measurement and rinsed beforehand with methanol

The various parts of the sampling train are cleaned in advance with methanol so that they are free of PFAS.

- Adsorbent: The adsorbent (XAD-2) is extracted overnight with methanol by means of a soxhlet extraction before sampling. Following extraction, the XAD-2 cartridges are dried at 40°C in an oven and stored (wrapped in aluminum foil) in a sealed glass jar. Additional cleaning steps by rinsing and/or extraction with water (as proposed in the OTM-45 revision[3]) and drying with nitrogen purge can be applied if required. XAD-2 cleaning is carried out maximum 1 week prior to sampling. The cartridges are filled with 20- 40 g of purified XAD-2, with a minimum aspect ratio of 2. Sampling standards (SS) are spiked inside the primary XAD-2 (13C3-PFBA,

[3] https://www.epa.gov/system/files/documents/2025-01/other-test-method-45-rev1-final-1-14-25.pdf

13C8-PFOA, 13C8-PFOS; Hamilton syringe) and filter (13C2-PFUnDA, 13C2-PFDoDA). For the cooled probe sampling train variant, 13C2-PFUnDA and 13C2-PFDoDA are not spiked on the filter, but inside the condensate flask. Typically, the XAD-2 pattern is doped with 10 ng of each standard. The XAD-2 is secured in the cartridge by means of purified glasswool.

- Glass wool: Glass wool is purified with methanol and dried at room temperature with N2.

3.2 SAMPLING

The sampling procedure is similar for the heated (§2.1) and cooled (§2.2) sampling train variants and consists successively of:

- Set up sampling train, perform a leak test and collect field blank samples (6, Appendix 1);
- Heating (or cooling) of probe and filter housing;
- Installation of the sampling probe in the gas duct;
- Register gas meter readings;
- Start the pump and set required isokinetic sampling flow rates;
- Isokinetic sampling of the gas duct for at least 3 hours (~2 Nm^3);
- Perform a new leak test after sampling to ensure that no leaks were created during the measurement.

The necessary attention must be paid to prevent the contents of the impingers from being sucked back as a result of underpressure in the gas duct or as a result of pressure variations in the sampling line when starting the pumps.

- Check the sampling flow rates regularly and adjust if necessary. Register the pressure, temperature, sampling flow rate and gas meter readings. If sampling is to be performed at different points (traverse), move the sampling probe from point to point without stopping the pump and set the sampling parameters depending on isokinetic sampling. When changing from measurement opening (flange), the pump must be switched off.
- Subsequently, the pump is stopped. Register the gas meter readings again. Remove the sampling probe from the gas duct.
- Proceed to the recovery of the field samples (7; §3.5)
- Rinse the glassware again and recover the post-rinse blank samples (2; § 6.1.1)

3.3 CONTROLS

The following checks are carried out during a stack measurement:

- Check the gas velocities at the sampling points and calculate the sampling parameters to be set at each point (flow rate, sampling duration) if necessary;
- Check the sampling train for leak-tightness before each sampling (see also procedure on essential quality requirements LUC/0/005);
- For each series of measurements and at least once a day, a field blank must be taken from the equipment;
- Install the probe in the gas duct and condition the sampling system for at least 10 minutes so that the entire sampling train is at operating conditions and check the proper functioning of the probe;
- During the measurement, check the temperature of:
    - Filter: the temperature at the filter (filter housing or directly in the outgoing gas flow) is 120±12°C (or minimal 10°C above stack temperature). Monitor the temperature of the filter during the chimney measurement;
    - XAD-2 cartridges: the temperature of the XAD-2 cartridges must be lower than 20°C for efficient capture of the target components.

- Recover the field samples immediately after removing the probe from the chimney;

3.4 OTHER PARAMETERS TO BE REGISTERED

To convert the quantified mass (ng/analysis fraction) into normalized stack emissions (ng/Nm³), it is necessary to measure additional stack parameters during the sampling period (LUC/0/005):

- Volume flow rate (m³) and temperature (°C) of the emitted gases, together with a continuous measurement of these parameters at a reference point if the flow rate is not constant.
- Water content (%)
- O_2 concentration (%)

3.5 RECOVERY AND AGGREGATION OF FIELD SAMPLES

Each emission measurement consists of 20 samples (S1-S20 in Appendix 1), including medium blank samples (5), field blank samples (6), field samples (7) and post-rinse blank samples (2). Aggregation of the heated probe field samples (S11-17 in Appendix 1) is explained below:

3.5.1 RECOVERY AND AGGREGATION OF HEATED PROBE SAMPLES

MeOH rinse fraction FRONT (S12 in Appendix 1): The glassware before the filter (nozzle, heated probe, tubing and front part of filter holder) is rinsed 3 times (in the field) with alkaline methanol (methanol/1% NH4OH) and this rinsing liquid is supplied to the laboratory in an HDPE recipient (S12).

Filter (S14 in Appendix 1): The loaded filter is removed from the sampling train and delivered to the laboratory in an aluminum-packed petri dish.

Water fraction (S17 in Appendix 1): The condensate from the condensate flask and the water from the impingers are transferred as a mixed sample into an HDPE recipient and delivered to the laboratory.

MeOH rinse fraction BACK (S15 in Appendix 1): The glassware after the filter (rear part of the filter holder, condenser, condensate flask, impingers and connectors) are rinsed 3 times with alkaline methanol (methanol/1% NH4OH) and delivered to the laboratory in an HDPE recipient (S15).

Cyclohexane rinse fraction (S13 in Appendix 1): After collecting the MeOH rinse (S12-15), the glassware from the nozzle up to and including the condensate flask (nozzle, probe liner, condenser, condensate flask and connectors/liner) are rinsed 3 times once more with cyclohexane and the rinsing liquid delivered to the laboratory in an HDPE recipient (S13).

XAD-2 (S16+S18 in Appendix 1): The XAD-2 cartridges are recovered from the sampling train. The cartridges are sealed at both sides using glass caps (or collected in an HDPE recipient) and supplied to the lab as separate samples (S16 and S18 in Appendix 1). As more data on breakthrough occurrence is collected, the analysis requirements of the XAD-2 cartridges as individual fractions may be relaxed.

3.5.2 RECOVERY AND AGGREGATION OF COOLED PROBE SAMPLES

If the cooled probe setup (§2.2) is applied, potential deposition of particle-bound PFAS in the condensate (S17.1) will be considered by carrying out an additional filtration of the water, after which the residue is added to the filter sample (S14*) and the filtrate is added to the water fraction (S17.2).

MeOH rinse fraction FRONT (S12 in Appendix 1): Het glassware up to and including the condensate flask is rinsed 3 times (in the field) with alkaline methanol (methanol/1% NH4OH) and this rinsing liquid is supplied to the laboratory in an HDPE recipient (S12).

Filter (S14 in Appendix 1): The loaded filter is removed from the sampling train and delivered to the laboratory in an aluminum-packed petri dish.

Water fraction condensate (S17.1 in Appendix 1): The condensate from the condensate flask (with potential dust fraction) is transferred into a cleaned HDPE recipient and delivered to the laboratory for filtration. After filtration by means of a quartz fiber filter, the filter residu is added to the filter sample (S14*) and filtrate (S17.1*) added to the water fraction of the impingers (S17.2).

Water fraction impingers (S17.2 in Appendix 1): The water from the impingers is transferred into a cleaned HDPE recipient and delivered to the laboratory.

MeOH rinse fraction BACK (S15 in Appendix 1): The glassware after the condensate flask up to the XAD-2 cartridges (impingers and connectors/liners) are rinsed 3 times (in the field) with alkaline methanol (methanol/1% NH4OH) and this rinsing liquid is supplied to the laboratory in an HDPE recipient (S15).

Cyclohexane rinse fraction (S13 in Appendix 1): After collecting the MeOH rinses (S12-15), the glassware from the nozzle up to (and including) the condensate flask (nozzle, probe liner, condenser, condensate flask and connectors/liners) is rinsed 3 times once more with cyclohexane and the rinsing liquid delivered to the laboratory in an HDPE recipient (S13).

XAD-2 (S16+S18 in Appendix 1): The XAD-2 cartridges are recovered from the sampling train. The cartridges are sealed at both sides using glass caps (or collected in an HDPE recipient) and supplied to the lab as separate samples (S16 and S18 in Appendix 1). As more data on breakthrough occurrence is collected, the analysis requirements of the XAD-2 cartridges as individual fractions may be relaxed.

All collected field samples are stored and transported in the dark (shielded from UV light) and cooled (~4°C). To avoid contamination of the media and field samples, special attention should be paid to hygiene during transport, field handling, sampling, recovery and laboratory analysis, as well as during the preparation of the XAD-2 cartridges. Each sampling results in 20 samples (Appendix 1) that are aggregated into 6 analytical fractions that are further processed and analyzed (Table 3).

Table 4 Aggregation of field samples into analytical fractions (F1-F6) for both the heated and cooled sampling train variant. The references of the field samples (S12-S18) refer to the described recovery of the field samples above (§3.5).

FRACTION	HEATED PROBE VARIANT	COOLED PROBE VARIANT
F1	Filter (S14) + MeOH rinse fraction FRONT (S12)	Filter (S14) + Residu filtration (S14*) + MeOH rinse fraction FRONT (S12)
F2	MeOH rinse fraction BACK (S15)	MeOH rinse fraction BACK (S15)
F3	Primary XAD-2 (S16)	Primary XAD-2 (S16)
F4	Water fraction (S17)	Water fraction: condensate filtrate (S17.1*) + impinger water (S17.2)
F5	Secondary XAD-2 (S18)	Secondary XAD-2 (S18)
F6	Cyclohexane rinse (S13)	Cyclohexane rinse (S13)

3.6 TRANSPORT AND STORAGE

All field samples are transported cooled (<6°C) and in the dark (shielded from UV light). In the laboratory, the analytical fractions (F1-F6) are stored in the dark and cooled (<6°C) and extracted within 28 days after sampling. The extracts can then be refrigerated (<4°C) and stored in the dark for up to 1 year.

Remarks:

- Contact with Teflon or other fluorine-containing polymers should be avoided.
- The concentration of >C10 PFAS in water samples can decrease with increasing storage time due to sorption to recipient walls or deposition (WAC/IV/A/025).

4 ANALYSIS PROCEDURE

In the lab, the aggregated analytical fractions (Table 4) are extracted for analysis (§4.2-4.6).

The quantitative analysis of the analytical fractions via LC-MS/MS (§4.7) is performed according to WAC/IV/A/025 for the semi-volatile (C4-C18) polar PFAS compounds and WAC/IV/A/026 for the most volatile (<C4) polar PFAS compounds. The mass of PFAS is calculated using the internal standard method. The per- and polyfluoroalkyl compounds and internal standards are identified based on the retention times and ion ratio criteria stated in WAC/VI/A/003.

If a high level of PFAS is expected, the samples can be pre-screened, e.g. through a non-target analysis. To this end, a small part (max 2%) of the XAD-2 cartridge and/or of the condensate is taken for analysis.

4.1 MATERIALS AND REAGENTS

For the material, reagents, standards and solutions used, refer to WAC/IV/A/025 and WAC/IV/A/026

4.2 EXTRACTION FILTER (FRACTION F1)

- Transfer the filter to a (PP) tube.
- Add an appropriate amount of the standard solution of internal standards (IS) so that the theoretical concentration of the IS in the extract is equal to that in the calibration standards.
- Add 10mL of the MeOH rinse fraction FRONT (S12), making sure the filter is completely submerged. Add additional alkaline methanol (MeOH/1% NH_4OH) if necessary. Evaporate the remaining MeOH rinse fraction FRONT (S12) to a few mL.
- Vortex
- Sonicate for 1 hour
- Decant the extract into another (PP) tube.
- Evaporate the extract to approximately 2 mL
- Centrifuge and transfer MeOH fraction to a new PP tube without taking over the filter residue
- Wash the filter residue with MeOH, vortex, centrifuge and transfer MeOH to the same PP tube
- This washing step is repeated once more
- Add the remaining rinsing liquid that was evaporated (a few mL).
- Evaporate extract to 500 µL (MeOH fraction). Vortex regularly to prevent the compounds from depositing on the wall of the test tube
- Add water or MeOH depending on the compounds of interest, i.e. the semi-volatile (C4-C18) or most volatile (<C4) polar PFAS; calibration standards are prepared with similar solvent ratios as the extracts;

Typically 10 µl of the extract is injected into the LC-MS.

The storage time of extracts is 1 month when stored in the refrigerator. Extracts that have been in the refrigerator are vortexed before injection.

4.3 EXTRACTION MEOH RINSE (FRACTION 2)

- If desired, the extract can be divided into 2 subfractions and one subfraction can be saved for reanalysis.
- Add an appropriate amount of the standard solution of internal standards so that the theoretical concentration of the internal standards in the measurement extract is equal to that in the calibration standards.
- Evaporate to approximately 2 mL
- The sample is transferred to a 15 mL PP tube and the recipient is rinsed 4 times with MeOH
- Further evaporation to 500 µL. Vortex regularly to prevent the compounds from depositing on the wall of the test tube
- Add water or MeOH depending on the compounds of interest, i.e. the semi-volatile (C4-C18) or most volatile (<C4) polar PFAS; calibration standards are prepared with similar solvent ratios as the extracts;

Typically 10 µl of the extract is injected into the LC-MS.

The storage time of extracts is 1 month when stored in the refrigerator. Extracts that have been in the refrigerator are vortexed before injection.

4.4 EXTRACTION OF THE XAD-2 CARTRIDGES (FRACTION F3 AND F5)

- If the primary XAD-2 cartridge contains visible water, purge it for 2 minutes under a N_2 flow. The drops of water from the cartridge are added to the water fraction (F4). Register the amount of purged water by pre- and post-weighing the XAD-2 cartridge. The secondary XAD-2 cartridge and blank XAD-2's do not contain water and can be extracted as such.
- Add an appropriate amount of the standard solution of internal standards within the XAD-2 by means of a Hamilton syringe so that the theoretical concentration of the internal standards in the measurement extract is equal to that in the calibration standards.
- Add 75 mL of MeOH/1% NH_4OH
- Close the cartridge on both sides with glass caps.
- Sonicate for 1 hour (in recipient filled with water up to the MeOH level)
- The glass caps are replaced by couplings and the extraction liquid is pushed out of the cartridge by means of a N_2 flow for 2 minutes and collected in a 500 mL recipient.
- Rinse XAD-2 with approximately 30mL MeOH, flush with N2 for 2 minutes and add to the rinsing liquid to the same recipient
- Rinse cartridge caps with a few mL of MeOH
- Evaporate the MeOH fraction to approximately 2 mL
- Transfer extract to 15 mL PP tube and rinse the recipient 4 times with MeOH
- Further evaporation to 5 mL
- Bring the extract over SPE (e.g. Phenomenex)
    - Condition the cartridge with subsequently 5mL ACN and 5mL of MeOH
    - Bring the extract over the SPE cartridge
    - Rinse the SPE cartridge with 2x 2.5mL ACN
- Evaporate the extract down to a few droplets, dilute to 1 mL, evaporate again to a few droplets, dilute once more to 1 mL, and finally evaporate to 500 µL. Meanwhile, vortex regularly to prevent the compounds from depositing on the wall of the test tube.
- Add water or MeOH depending on the compounds of interest, i.e. the semi-volatile (C4-C18) or most volatile (<C4) polar PFAS; calibration standards are prepared with similar solvent ratios as the extracts;

Typically 10 µl of the extract is injected into the LC-MS.

The storage time of extracts is 1 month when stored in the refrigerator. Extracts that have been in the refrigerator are vortexed before injection.

4.5 EXTRACTION WATER FRACTION (FRACTION 4)

- Determine the total weight of the water fraction from the XAD-2 cartridge, the condensate and the impinger water.
- The sample bottles are first emptied and then rinsed with sufficient methanol (< 10% methanol), after which the water and methanol are combined before taking a subsample. In this case, the laboratory states on the report that the analysis was carried out on a sub- sample.
- Take a subsample, e.g. 25 mL of the water fraction from the XAD-2 cartridge and condensate and 25 mL of the impinger fraction and combine them (2*25 mL).
- The remainder of the water fractions (XAD-2 water, condensate and impinger water) can be saved for reanalysis.
- Add an appropriate amount of the standard solution of internal standards so that the theoretical concentration of the IS in the measurement extract is equal to that in the calibration standards.

- Vortex the mixture vigorously.
- To extract the sample, use Solid Phase Extraction (SPE) with a SPE-WAX cartridge (e.g. OASIS WAX 6mL, 150mg) for the semi-volatile (C4-C18) compounds under WAC/IV/A/025. For the most volatile (<C4) compounds under WAC/IV/A/026, apply a Phenomenex cartridge. The SPE procedure includes the following steps:
    - Condition the SPE cartridge with 4 mL MeOH/0.1% NH_4OH solution;
    - Condition the SPE cartridge with 4 mL of methanol;
    - Condition the SPE cartridge with 4 mL of MQ water;
    - Transfer the subsample (50 mL) over the SPE cartridge;
    - Centrifuge the SPE cartridges so that they are dry (20 min, 2000+ rpm)
    - Rinse the sample recipient with 5 mL methanol and use it to elute the SPE cartridge; capture this fraction;
    - Rinse the sample recipient with 5 mL MeOH/0.1% NH4OH solution and use it to elute the SPE cartridge; combine this fraction with the previous one;
- The SPE extract is evaporated to 500 µL. Vortex regularly to prevent the compounds from depositing on the wall of the test tube
- Add water or MeOH depending on the compounds of interest, i.e. the semi-volatile (C4-C18) or most volatile (<C4) polar PFAS; calibration standards are prepared with similar solvent ratios as the extracts;

Typically 10 µl of the extract is injected into the LC-MS.

The storage time of extracts is 1 month when stored in the refrigerator. Extracts that have been in the refrigerator are vortexed before injection.

4.6 Extraction of cyclohexane rinse (Fraction 6)

- If desired, the mixture can be divided into 2 subfractions and one subfraction can be saved for reanalysis.
- Add an appropriate amount of the standard solution of internal standards so that the theoretical concentration of the internal standards in the measurement extract is equal to that in the calibration standards.
- Evaporate to approximately 2 mL
- The samples are transferred to 15 mL PP tubes and the recipient is rinsed 4 times with MeOH
- Further evaporate to a few drops. Vortex regularly to prevent the components from depositing on the wall of the test tube
- Add MeOH until 500 mL
- Add water or MeOH depending on the compounds of interest, i.e. the semi-volatile (C4-C18) or most volatile (<C4) polar PFAS; calibration standards are prepared with similar solvent ratios as the extracts;

Typically 10 µl of the extract is injected into the LC-MS.

The storage time of extracts is 1 month when stored in the refrigerator. Extracts that have been in the refrigerator are vortexed before injection.

4.7 LC-MS/MS MEASUREMENT

The LC-MS/MS measurement is performed according to WAC/IV/A/025 for the semi-volatile PFAS and WAC/IV/A/026 for the most volatile (<C4) polar PFAS. Examples of appropriate LC- and MS-conditions are found in the respective compendium procedures.

5 REPORTING

The analytical report consists of the measured mass concentrations per analytical fraction (ng/fraction) for the field sample and field blank (<10%) and the resulting relative breakthrough of the secondary XAD-2 cartridge (<30%). The emission concentration ($C_{emission}$) of each compound (summed over the different analytical fractions) is then calculated in ng/Nm³. This is calculated from the sum concentration of the samples (analyzed fractions), normalized by the amount of sampled air (Nm³) and the prevailing O_2 concentration in the chimney. When calculating the sum of the mass fractions (ng), the lower bound method ("lower bound": <LOQ = 0) is applied in accordance with WAC/IV/A/025.

The sampling volume (V_samp) is calculated from the monitoring data of the gas meter, temperature and pressure meter according to:

$$V_{samp} = \frac{(V_{end} - V_{start}) * 273{,}15 * P_{gas}}{(273{,}15 + T_{gas}) * 1013{,}25}$$

with V_{samp} the sampling volume (Nm³dr), V_{start} and V_{end}, respectively, the start and end volume as monitored by the gas counter (m³), P_{baro} the absolute pressure (mbar) at the gas counter and T_{gas} the temperature at the gas counter (°C). Furthermore, 273.15 is the reference temperature (Kelvin) and 1013.25 is the reference pressure (mbar).

The quantified fraction masses (ng/fraction) are then summed over the different analysis fractions according to the lower bound method (<LOQ = 0) and finally normalized for the sampled flow rate (V_{samp} in Nm³) and the oxygen level (O_2 in %) to obtain the emission concentration ($C_{emission}$ in ng /Nm³) to obtain:

$$C_{emission} = \frac{C_{mon}}{V_{samp}} * [\frac{(21 - O_{2\ REF})}{(21 - O_{2\_stack})}]$$

with $C_{emission}$ the normalized emission concentration (ng/Nm³ dr), C_{mon} the summed fraction masses (ng) following the lower bound method (<LOQ = 0), O_{2_REF} the reference oxygen content (11%) and O_{2_stack} the oxygen content in the stack (%).

6 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLING

6.1.1 SAMPLING BLANKS

Due to the contamination risk, strict quality control procedures are provided in this LUC procedure. This follows the OTM-45 quality procedure, but relaxes the blank use depending on the glassware use. Three types of sampling blanks are considered:

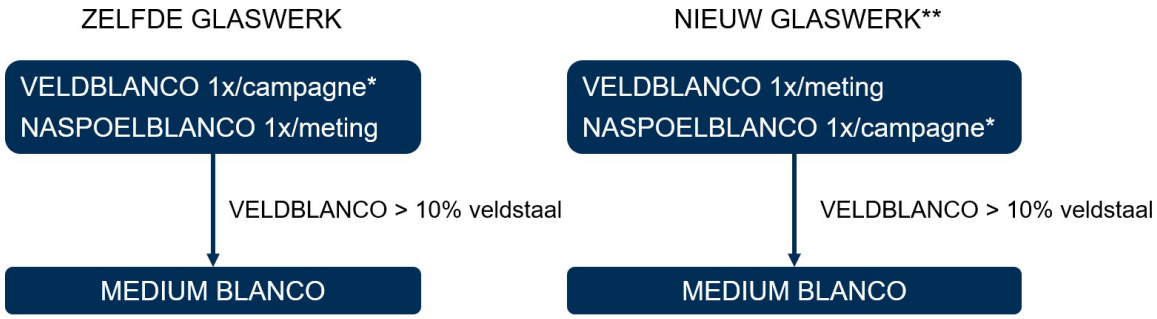
- **Medium blank (S1-S5 in Appendix 1):** A blank filter, rinsing fluid (alkaline methanol and cyclohexane), blank XAD-2 and ultrapure water (5 samples) are supplied to the laboratory in HDPE containers. Nothing has been done in the field with this blank, just a transfer to the sampling container in the lab. The purpose of the media blank is to determine whether spent media or other interferences are introduced into the sample through transportation, storage, and the field environment.
- **Field blank (S6-S11 in Appendix 1):** The entire sampling train is assembled, the filter house is heated, a leak test conducted and, subsequently, rinsed with alkaline methanol just before sampling. Recovery and aggregation of the field samples follows the same procedure as described in §3.5, with the exception of the secondary XAD-2 cartridge. The resulting analytical fractions (6) are delivered to the laboratory in an HDPE container:
    - S6: MeOH rinse fraction FRONT
    - S7: Filter
    - S8: XAD-2 (primary only)
    - S9: Impinger water
    - S10: MeOH rinse fraction BACK
    - S11: Cyclohexane rinse

  The measured field blank concentrations in each fraction are also reported for interpretation of the analytical results.
- **Post-rinse blank (S19-S20 in Appendix 1):** After collecting the field samples (S12-S18), the glassware is rinsed again 3 times with alkaline methanol (S19) and 3 times with cyclohexane (S20). The rinses are combined per solvent and delivered to the laboratory in HDPE recipients (methanol (S19) and cyclohexane (S20)). The purpose of the post-rinse blank is to check whether all PFAS have been adequately captured in the field samples.

The different sampling blanks are collected during each campaign (maximum 3 consecutive measuring days at the same measuring location/company*) or measurement, depending on the glassware use (schedule):

- If similar glassware is used for each measurement, only 1 field blank needs to be collected per campaign, and a post-rinse blank for each measurement.
- If new glassware is used for each measurement, a field blank is required for each measurement and a post-rinse blank per measurement campaign.

To avoid unnecessary lab analysis of medium blanks (4 samples), LC-MS/MS analysis is only required when field blank results exceed 10% of the field sample. When a new stack is sampled at the same location/site, the use of new glassware is required.



*Campagne = max. 3 opeenvolgende meetdagen op eenzelfde meetlocatie

**Nieuwe Schoorsteen = nieuw glaswerk

6.1.2 SAMPLING STANDARDS (SS)

For each stack measurement, isotope-labeled sampling standards (SS) are added to the primary XAD-2 (^{13}C8-PFOA, ^{13}C8-PFOS ^{13}C3-PFBA) and filter (^{13}C2-PFUnDA, ^{13}C2-PFDoDA) to control for the entire sampling and analysis process. In this LUC method, sampling standards for C4 (13C3-PFBA), C8 (13C8-PFOA and 13C8-PFOS) and >10C (^{13}C2-PFUnDA, ^{13}C2-PFDoDA) compounds are considered. The recoveries of these standards, after correction for the recovery of the internal standards (IS), must demonstrate per stack measurement that recovery of the labeled standards meets the required range of 70-130%. Between 50-70% recoveries are still acceptable, but recoveries must be flagged and reported. Below 50% standard recovery, the reason must be investigated and a new measurement might be required.

The percentage recovery (%) should be evaluated on the entire sampling train (sum of analysis fraction recoveries), as migration of the recovery standards throughout the train compartments cannot be excluded.

6.1.3 RELATIVE BREAKTHROUGH

The relative breakthrough (RD; %) of PFAS through the sampling train is evaluated per compound based on the mass ratio between the secondary (breakthrough) XAD-2 cartrigde (F5) and the sum of all fractions (F1-F6) in the sampling train via the following formula:

$$RD(\%) = \frac{F5_{mass}}{(F1_{mass} + F2_{mass} + F3_{mass} + F4_{mass} + F5_{mass} + F6_{mass}} x\ 100\%$$

If the relative breakthrough is lower than 30%, the quantified mass for each PFAS compound from fraction F5 (secondary XAD-2 cartridge) is added to the other fractions to calculate the total PFAS emission concentrations. If the relative breakthrough is greater than 30%, the reason must be investigated and, if necessary, a new measurement might be required.

7 MATERIAL

7.1 SAMPLING

- Heated probe + filter housing
- Quartz fiber filter
- Uniquely engraved glassware + couplings (possibly with glass ball couplings):
    - Condenser
    - Condensation flask (1)
    - Impingers (2)
    - XAD-2 cartridges (2), spiked with sampling standards (SS)
- Teflon/PP/PE tubing (if necessary)
- Drying column with silica
- Pump
- Cooling bath with pump
- Aluminium foil
- Refrigerator box with ice (storage of field samples)
- Solvents: alkaline methanol (methanol/1% NH4OH) and cyclohexane
- Sufficient HDPE containers (28)

8 ADDITIONS OR DEVIATIONS FROM OTM-45

Based on the acquired practical experience of the reference laboratory with PFAS stack measurements, comparative measurements and bilateral communication with the Environmental Protection Agency (EPA) and Flemish commercial laboratories, a list of allowed deviations from the OTM-45 method (§8.1) and 2 alternative sampling trains (cooled probe) are defined (Hofman et al., 2025b).

8.1 DEVIATIONS

An overview of the allowed deviations of this method compared to the OTM-45 procedure, with associated arguments, is shown in Table 5.

Table 5 Overview of additions or deviations from the OTM-45 method

OTM-45	LUC
SAMPLING	
Heated sampling line between filter holder and condenser	No need for heated line between filter holder and condenser
Condensate guided through primary XAD-2 cartridge	The primary XAD-2 cartridge is configured in the back of the sampling train + additional sampling train variant (cooled probe)
Analytical fractions (4): • filter + front half rinse • back half rinse + primary XAD-2 • condensate + rinse condensate flask + impinger water + impinger rinse • secondary XAD-2	analytical fractions (6): • filter + front half rinse • primary XAD-2 • backl half rinse + condensate flask rinse • condensate + impinger water + impinger rinse • secondary XAD-2 • cyclohexane rinse
medium blanks collected in every measurement campaign and field nad post-rinse blanks collected for every measurement	Based on the observed blank concentrations, relaxation of blank collection frequency depening on the glassware use.
Cooled XAD-2 cartridges	XAD-2 cartridges are only cooled when temperature requirements (<20°C) cannot be fulfilled.
The OTM-45 method foresees A condensate flask and 3 additional impingers	Based on breakthrough tests in the water fraction, the amount of water was reduced by 100 mL (1 impinger) for both the heated and cooled probe variants: 1 condensate bottle and 2 impingers.
Concentration of ammonia in methanol is 5%	Concentration of ammonia in methanol can be lowered from 5% to 1%
Filter quality control (3 filters/batch) including extraction/prep. (§7.1.1.1)	Filter QC included in medium blank
Adsorbent (XAD-2) QC including sample extraction/prep (§7.1.3)	Adsorbent QC included in medium blank
Minimum sampling volume of 3 Nm^3 dr (§8.1.2.1)	Sometimes hard due to underpressure train: minimum 3h of monitoring (~2 Nm^3 dr)
Record color (condition) of silicate towers in field report (§8.2.10)	Not required
Rinse blank (Sample Train Field Blank STFB) again consists of a complete used sampling train with new media.	Post-rinse blank consists of a single rinse to check the sampling train
Temperature of the filter (120°C) is measured in the gas flow	Temperature can also be monitored in filter housing
The 1st, 3rd and 4th impinger are of the Greenburg-Smith type with a modified (longer) tip. Only the 2nd impinger is of the Greenburg-Smith type.	Alle impingers are of the standard type
Recovery of filter in glass petri dish closed with HDPE tape or resealable PE bag.	Filter is recovered in a petridish wrapped in aluminum foil
Before use, rinse aluminum foil three times with 5% ammonium hydroxide in methanol and store in a cleaned Petri dish or gauze jar.	After initial laboratory testing, this procedure is no longer used.
Recovery XAD-2 in original container, HDPE container with PP or PE lid or in glass container closed with glass lids.	Recovery XAD-2 in glass container or HDPE jar
Clean glass wool by immersing it 3 times in 5% ammonium hydroxide in methanol, drying in the oven at 110°C and storing in 5% ammonium hydroxide in methanol rinsed glass jar with PE or PP liner lid.	Glass wool is rinsed with methanol and dried with N2 at room temperature
Ammonium hydroxide, 5% in methanol rinse	After initial laboratory testing, the ammonia percentage can be reduced to 1%
Glassware washing procedure: Hot water + soap - tap water - deionized water - acetone, dichloromethane, methanol - drying at 300°	New glassware: Glassware is rinsed with warm water and methanol and fired for at least 3 hours at +/- 150°C Glassware used: Successively 1 hour sonication with methanol, 1 hour sonication with cyclohexane (fully immersed) and at least 3 hours firing at 450°C.
Seal glassware with glass lids or cleaned aluminum foil	Glassware is stored in a closed container
Rinse glassware again with 5% ammonium hydroxide in methanol before use	Only rinsed with methanol

Filter temperature is maintained at 120°C or 10°C above chimney temperature to prevent condensation on the filter.	Filter housing is kept at 120± 12 °C
Use a brush while rinsing the probe to collect any deposited material.	Only rinsing is applied (No contamination of rinse blanks observed)
SAMPLE PREP/ANALYSIS	
7 sampled samples are aggregated into 4 analytical fractions.	7 sampled samples are aggregated into 5 analytical fractions.
Recovery standards for C8 PFOA and PFOS (13C8-PFOA, 13C8-PFOS)	In addition to standard recoveries for C8 PFOA and PFOS (13C8-PFOA, 13C8-PFOS), also a spike from a C4 component (13C3-PFBA) in the XAD-2 and long-chain PFCAs (13C2-PFUnDA en 13C2-PFDoDA) on the filter (heated probe variant) or condensate (cooled probe variant)
18u shaking before extraction.	Following intial lab tests: 1h of sonication can be applied as alternative (+4x shaking)
dilution with water (or methanol) during evaporation	Dilute with methanol during evaporation
Analysis of PFAS compounds (50) described in OTM-45	Analysis of the PFAS components performed via LC-MS/MS analysis in accordance with WAC/IV/A/025 and WAC/IV/A/026. This methodology was validated for 52 components.
QC/ REPORTING	
If the relative breakthrough is greater than 10%, the fraction of the sec XAD-2 is added to the sum of the other fractions and reported.	The secondary XAD-2 cartridge concentration is always added to other fractions. Only if >30% should the reason be investigated and a re-measurement may be necessary if necessary.

9 REFERENCES

Other test Method 45 (OTM-45): Measurement of selected Per- and Polu fluorinated alkyl substances from stationary sources, Revision 0 (1/13/2021). https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf

Compendium voor de monsterneming, meting en analyse van lucht (LUC), LUC/0/005, Essentiële kwaliteitseisen voor emissiemetingen, https://emis.vito.be/nl/erkende-laboratoria/lucht-gop/compendium- luc

Compendium voor de monsterneming, meting en analyse van water (WAC), WAC/VI/A/003: Kwaliteitseisen voor de analysemethoden, https://emis.vito.be/nl/erkende-laboratoria/water-gop/compendium-wac

Compendium voor de monsterneming, meting en analyse van water (WAC), WAC/VI/A/025: Kwaliteitseisen voor de analysemethoden, https://emis.vito.be/nl/erkende-laboratoria/water-gop/compendium-wac

HOFMAN, J., BAEYENS, B., AERTS, W., JACOBS, G., DE CARVALHO, A. R., VAN DEN BERGH, G., VOORSPOELS, S. & OTTEN, G. 2025a. Quantification of per- and polyfluoroalkyl substances (PFAS) in air emissions: An interlaboratory comparison. Chemosphere, 380, 144449.

HOFMAN, J., JACOBS, G., BAEYENS, B., DE CARVALHO, A. R., AERTS, W., VOORSPOELS, S., DEN BERGH, G. V., DEUN, M. V., BERGHMANS, P., BRECHT, A. V. & OTTEN, G. 2025b. Quantifying per- and polyfluoroalkyl substances (PFAS) in air emissions: Lab & field experiences from a hazardous waste incinerator. Environment International, 109541.

10 APPENDIX

Appendix 1: Different samples originating from a PFAS emission measurement campaign, including medium blank, field blank and post-rinse blank.

S1	MEDIUM BLANK	Blank filter
S2		Blank rinse fraction MeOH
S3		Blank rinse fraction Cyclohexane
S4		Blank XAD-2
S5		Blank water
S6	FIELD BLANK	MeOH rinse fraction FRONT – Field blank
S7		Filter- Field blank
S8		XAD-2-1+spike- Field blank
S9		Impinger water - Field blank
S10		MeOH rinse fraction BACK - Field blank
S11		Cyclohexane rinse fraction - Field blank
S12	FIELD SAMPLE	MeOH rinse fraction FRONT (MeOH)
S13		Rinse Cyclohexane (Cyclohex)
S14		Filter
S15		MeOH rinse fraction BACK (MeOH)
S16		Primary XAD-2 (SS spike)
S17		Water fraction
S18		Secondary XAD-2
S19	POST-RINSE BLANK	MeOH post-rinse fraction
S20		Cyclohexane post-rinse fraction

Appendix 2: Applied sampling standards (SS)

		COMPONENT	
SS	SS1	Perfluoro-n-(13C8)octanoic acid (M8PFOA)	$^{13}C_8$-PFOA
	SS2	Sodium perfluoro-1-[13C8]octanesulfonate (M8PFOS)	$^{13}C_8$-PFOS
	SS3	Perfluoro-n-(2.3.4-13C3) butanoic acid (M3PFBA)	$^{13}C_3$-PFBA
	SS4	Perfluoro-n-[1,2-13C2]-undecanoic acid (M2PFUdA)	$^{13}C_2$-PFUnDA
	SS5	Perfluoro-n-[1,2-13C2]-dodecanoic acid (M2PFDoA)	$^{13}C_2$-PFDoDA

Note:
Variants of some isotopically labeled compounds are also available (e.g., 13C4-PFBA, 13C4-PFOA, 13C8-PFOS, 13C9-PFUnDA, 13C12-PFDoDA, etc.). These variants may also be used instead of the compounds listed above, as long as the sampling standards differ from the internal standards used (WAC/IV/A/025).