Determination of the concentration of 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 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 (semi-)volatile and particle-bound PFAS (boiling point >100°C, >C4) via LC-MS/MS analysis of samples resulting from a sampling train (see schematic representation in Figure 1):

- Probe rinse and filter holder rinse
- Filter
- Condenser rinse
- XAD2 cartridges: 1 at the beginning (primary) and 1 at ethe end (secondary/breakthrough) of the sampling train
- Condensate from condensate flask
- Impinger water
- Impinger rinse

The procedure is initially aimed at the quantitative analysis of 19 PFAS compounds that were subject to a validation test based on 3 repeated measurements (+ field blank; see §2.1) at a background location in Mol (nearest PFAS immision measurement in Dessel: 0.012 and 0.003 ng/m³ for, respectively, total and EFSA4). The sampling train was equipped with media (filter/XAD2 cartridge/impinger water) that were spiked with native PFAS (50 cpds) to a representative level. The associated measurement uncertainty (U, k=2) according to WAC/VI/A/002 for each of these compounds is shown in Table 1. For quantitative analysis, a U of <50% and total train recovery of 70-130% are required. A LOQ determination was performed per analysis fraction based on a low calibration standard with S/N ratio of 6 and, if necessary, increased based on the procedure blank concentration. The resulting LOQs were calculated per analysis fraction and 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 branched isomers (T-).

COMPONENT	CAS	U (k=2)	REC (%)	LOQ*			
				Filter + rinse	XAD2*	Water	Rinse
		%	*%*	*ng*	*ng*	*ng*	*ng*
PFBA	375-22-4	14%	103%	0.07	0.46	0.07	0.06
PFPeA	2706-90-3	11%	104%	0.07	0.3	0.06	0.05
PFHxA	307-24-4	10%	104%	0.14	0.24	0.17	0.108
PFHpA	375-85-9	11%	105%	0.07	0.14	0.22	0.05

L-PFOA	335-67-1	11%	105%	0.06	0.3	0.06	0.05
T-PFOA	335-67-1	9%	104%	0.06	0.32	0.06	0.05
PFNA	375-95-1	11%	108%	0.06	0.34	0.06	0.05
PFDA	335-76-2	15%	111%	0.07	0.42	0.06	0.05
PFUnDA	2058-94-8	14%	112%	0.07	0.38	0.06	0.05
PFDoDA	307-55-1	14%	111%	0.07	0.34	0.06	0.05
4:2FTS	757124-72-4	12%	96%	0.07	0.09	0.07	0.05
8:2FTS	39108-34-4	12%	108%	0.07	0.07	0.06	0.06
L-MePFOSAA	2355-31-9	6%	101%	0.07	0.07	0.06	0.05
T-MePFOSAA	2355-31-9	6%	99%	0.07	0.07	0.06	0.05
L-EtPFOSAA	2991-50-6	3%	101%	0.07	0.07	0.06	0.05
T-EtPFOSAA	2991-50-6	3%	100%	0.07	0.07	0.06	0.05
HFPO-DA	13252-13-6	17%	100%	0.1	0.1	0.1	0.1
ADONA	919005-14-4	14%	101%	0.06	0.06	0.06	0.05
PFECHS	646-83-3	26%	85%	0.06	0.06	0.06	0.05

** For the XAD2 fraction, the LOQ was increased based on the field blank as the procedure blank showed elevated concentrations for a number of compounds. The LOQs listed here are based on 1 validation experiment. LOQs must be recalculated and evaluated with each new measurement.*

At the same time, the compounds in Table 2 (22) can be determined indicatively (Table 2). In the validation exercise, the sulfonates (PFBS-PFDS in Table 2) met a measurement uncertainty of <50% and total train recovery of 70-130%. However, these results were not reproduceable in a new validation test. These compounds are therefore included as indicative for the time being.

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 branched isomers (T-).

COMPONENT	CAS	U (k=2)	REC (%)	LOQ*			
		%	%	Filter + rinse ng	XAD2* ng	Water ng	Rinse ng
PFTrDA	*72629-94-8*	*38%*	*101%*	0.07	0.24	0.06	0.05
PFTeDA	*376-06-7*	*68%*	*85%*	0.07	-	0.06	0.05
PFHxDA	*67905-19-5*	*104%*	*79%*	0.05	-	0.04	0.1
PFODA	*16517-11-6*	*105%*	*62%*	0.05	-	0.11	0.1
PFBS**	*375-73-5*	*19%*	*107%*	0.07	0.2	0.06	0.05
PFPeS**	*2706-91-4*	*10%*	*101%*	0.06	0.1	0.06	0.05
L-PFHxS**	*355-46-4*	*13%*	*106%*	0.06	0.1	0.06	0.05
T-PFHxS**	*355-46-4*	*12%*	*104%*	0.06	0.1	0.06	0.05
PFHpS**	*375-92-8*	*14%*	*97%*	0.06	0.1	0.06	0.05
L-PFOS**	*1763-23-1*	*8%*	*104%*	0.68	1.3	0.56	0.46
T-PFOS**	*1763-23-1*	*8%*	*103%*	1.02	2	0.86	0.7
PFNS**	*68259-12-1*	*18%*	*98%*	0.07	0.2	0.06	0.05
PFDS**	*335-77-3*	*37%*	*89%*	0.07	0.2	0.06	0.05
PFUnDS	*749786-16-1*	*60%*	*81%*	0.07	0.2	0.06	0.05
PFDoDS	*79780-39-5*	*96%*	*70%*	0.07	0.2	0.06	0.05

PFTrDS	*791563-89-8*	*104%*	*74%*	0.07	0.2	0.06	0.05
6:2FTS	*27619-97-2*	*48%*	*64%*	0.07	0.32	40	0.05
10:2FTS	*120226-60-0*	*14%*	*108%*	0.06	0.1	0.06	0.05
L-PFOSA	*754-91-6*	*70%*	*72%*	0.07	0.1	0.15	0.2
T-PFOSA	*754-91-6*	*72%*	*71%*	0.07	0.1	0.15	0.2
6:2diPAP	*57677-95-9*	*51%*	*90%*	0.07	0.1	0.06	0.05
6:2/8:2diPAP	*943913-15-3*	*85%*	*75%*	0.07	0.1	0.06	0.05

**For the XAD2 fraction, the LOQ was increased based on the field blank as the procedure blank showed elevated concentrations for a number of compounds. The LOQs listed here are based on 1 validation experiment. LOQse must be recalculated with each new measurement.*
***Although these compounds met the measurement uncertainty and recovery citeria in the validation test initially, recovery problems (<30%) were later identified for the sulfonic acids. These are now further investigated.*

2 PRINCIPLE & SETUP

For the measurement of PFAS (>C4, boiling point >100°C) in emissions, a sampling train is used based on EPA's OTM-45 method (published 1/13/2021) and as shown in Figure 1. This OTM-45 method was published by EPA to promote consistency in the sampling and analysis of PFAS in conducted emissions and is considered best available technology. Gaseous and particulate PFAS (>C4, boiling point >100 °C) are sampled isokinetically (same magnitude and direction of gas velocity) from the chimney using a heated probe. Particle-bound PFAS are collected on a heated glass wool or quartz filter (120 °C or at least 10 °C above chimney temperature), after which gaseous PFAS are captured via a primary adsorbent (XAD-2) cartridge, a condensation bottle, a series of impingers with absorption reagent (ultrapure water) and then a secondary adsorbent (XAD-2; breakthrough) cartridge.

2.1 OTM-45 SAMPLING TRAIN

The OTM-45 sampling train is shown in Figure 1 and consists of:

- a heated probe with quartz or glass wool filter
- a condenser
- a primary adsorbent (XAD-2) cartridge
- a condensate flask
- a series of 3 impingers filled with ultrapure water
- a secondary adsorbent (XAD-2) cartridge (breakthrough)
- a drying tower (silica or equivalent desiccant) with pump

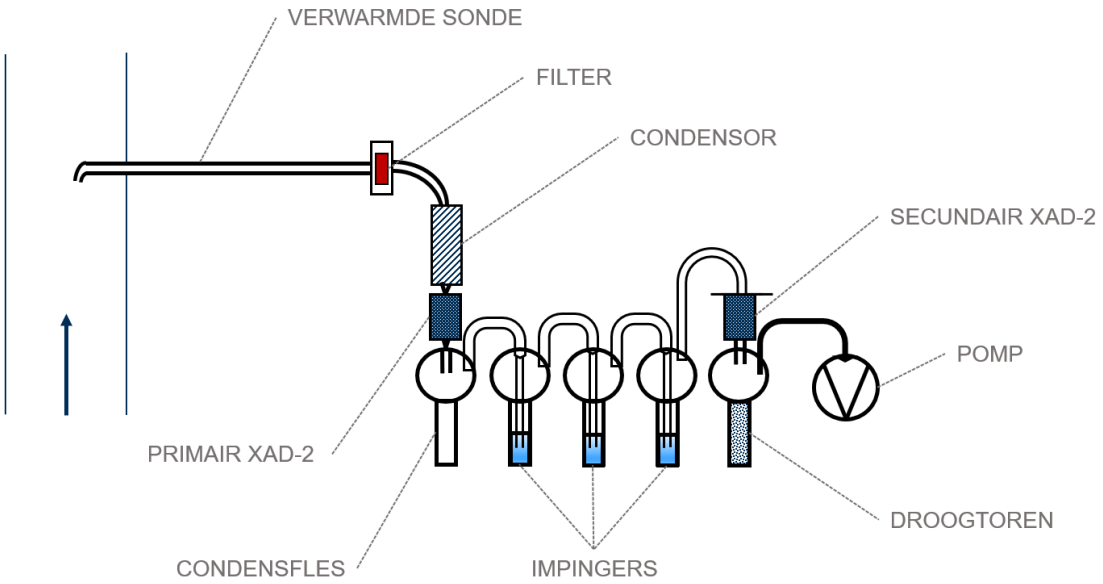


Figure 1 Schematic representation of OTM-45 sampling train

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. Polypropylene (PP) or polyethylene (PE, HDPE) products can be used to replace PTFE. Any contamination in the media or sampling train used can be determined in the respective 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 during the chimney measurement to avoid condensation/moisture on the filter. This temperature must be measured in the filter housing.
- Tubing, condenser, and XAD2 cartridges should be oriented vertically in the sampling train to facilitatate maximal flow and avoid moisture buildup inside the train compartments.
- 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 100ml of ultrapure water

Recovery of the samples takes place in existing cartridges (e.g. Table 2).

Since the condensate in the sampling train described above is sent through the primary XAD-2, the adsorbent cartridge can become very wet in stacks with a high moisture content. This could possibly

have an effect on the capture efficiency of the adsorbent cartridge or the required underpressure in the sampling train. Two alternative sampling trains were therefore defined in which the condensate is collected in a condensate flask before the sampled gas flow is sent through the XAD2 cartridge, namely the OTM-45 variant (§8.2.1) and the cooled probe method (§8.2.2). The equivalence of these sampling variants was demonstrated for 3 PFAS compounds (PFBA, T-PFOA and PFHxA; C4-C8) by means of simultaneous stack measurement with multiple laboratories (interlaboratory test). The equivalence of these sampling trains will be further investigated for the entire WAC/IV/A/025 scope by means of a new interlaboratory test in 2024.

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. Glass liners (probe) 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 a maximum of 2 weeks before sampling, then rinsed with methanol and dried at 150°C. Pending sampling, the glassware is stored in a closed container.
- The glass probe liner is rinsed with methanol

The following applies to existing glassware that is reused:

- The glassware (except liner) is cleaned with warm water a maximum of 2 weeks before sampling and rinsed successively with methanol and cyclohexane.
- After cleaning with methanol and cyclohexane, the glassware is oven dried at at least 450°C for at least 3 hours. The glassware is now ready for sampling. Pending sampling, the glassware is stored in a closed container.
- Glass liners (probe) are replaced with each measurement and rinsed with methanol beforehand

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 (16 hours) with methanol by means of a soxhlet extraction before sampling. Afterwards, the XAD-2 cartridges are dried at 40°C in an oven and stored (wrapped in aluminum foil) in a sealed glass jar. The cleaning of the XAD-2 is carried out a maximum of 1 week before sampling. The cartridges are filled with 20-40 g of purified XAD-2, with a minimum aspect ratio of 2. The recovery standards (13C3 PFBA, 13C8 PFOA, 13C8 PFOS) are added to the primary Typically the XAD-2 pattern is doped with 30 µg of each standard. The XAD-2 is secured in the cartridge by means of purified glass wool.
- Glass wool: Glass wool is purified with methanol and dried at room temperature with N2.

3.2 SAMPLING

The sampling procedure depends on the sampling train used (OTM-45 (§2.1), OTM-45 variant (§8.2.1) or cooled probe variant (§8.2.2)) and consists successively of:

- Set up a 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 probe in the gas duct;
- Registering gas meter readings;
- Starting the pump and setting required isokinetic suction flow rates;
- Sampling of the exhaust 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 a negative pressure in the gas channel or as a result of pressure variations in the sampling line when starting the pumps.

- Check the flow rates regularly and adjust them if necessary. Register the pressure, temperature, flow rates 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 the measuring opening, the pump must be switched off.
- Then the pump is stopped. Register the gas meter readings again. Remove the probe from the gas channel.
- Proceed to the recovery of the field samples (11; §3.5)
- Rinse the glassware again and recover the post-rinse blank samples (6; § 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 essential quality requirements LUC/0/005);
- For each series of measurements and at least once a day, a blank must be taken from the equipment (field blank);
- Install the probe in the gas channel 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 inspection measurement, check the temperature of:
- Filter: the temperature at the filter (filter housing or directly in the outgoing gas flow) is 120±12°C. 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/Nm^3), it is necessary to measure additional stack parameters during the sampling period (LUC/0/005):

- Volume flow rate (m^3) 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

For each emission measurement, 28 samples are collected (Appendix 1), including medium blank samples (5), field blank samples (6) and post-rinse blank samples (6). Treatment of the field samples (S12-22 in Appendix 1) is explained below:

Probe rinse + front half rinse (S12 + S13 in Appendix 1): After sampling (in the field), the front part of the filter holder and probe are rinsed 3 times with alkaline methanol (methanol/1% NH4OH) and this rinsing liquid is supplied to the laboratory in an HDPE container (S12). This rinse is repeated again (3x) with cyclohexane and delivered to the laboratory in a separate HDPE container (S13). With the cooled probe method (§8.2.2), the rinses from the probe and filter holder are recovered as separate field samples (S12_1 and S12_2).

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.

Back half rinse to the condenser (S15 + S16 in Appendix 1): From the rear part of the filter holder up to and including the condenser is rinsed 3 times after sampling (in the field) with alkaline methanol (methanol/1% NH4OH) and delivered to the laboratory in an HDPE container (S15). This rinse is repeated again (3x) with cyclohexane and delivered to the laboratory in a separate HDPE container (S16).

Condensate (S18 in Appendix 1): The condensate from the condensate flask is transferred to a cleaned HDPE container and delivered to the laboratory.

Rinse of condensate flask (S19 in Appendix 1): The condesate flask is rinsed 3 times with alkaline methanol (methanol/1% NH4OH) and delivered to the laboratory in an HDPE container.

Impinger water (S20 in Appendix 1): The water from the impingers is transferred as a mixed sample into a cleaned HDPE container and delivered to the laboratory.

Impinger rinse (S21 in Appendix 1): The impingers are rinsed 3 times with alkaline methanol (methanol/1% NH4OH) and delivered to the laboratory in an HDPE container.

XAD-2 (S17+S22 in Appendix 1): The XAD2 cartridges are recovered from the sampling train. The cartridges are closed at both sides using cut glass caps (or collected in an HDPE jar) and are supplied to the lab as separate samples (17 and 22 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.

If the cooled lance probe setup (§8.2.2) is applied, any deposition of particulate PFAS in the condensate will be taken into account by carrying out an additional filtration of the condensate, after which the residue is added to the filter sample (S14*) and the filtrate is added to the condensate sample (S18*). In addition, the probe and filter holder are rinsed separately with methanol and cyclohexane and delivered to the laboratory as separate rinses (S12_1 and S12_2).

All collected field samples are stored and transported in the dark (shielded from UV light) and on ice (~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 28 samples (Appendix 1) that are aggregated into 6 analytical fractions that are further processed and analyzed (Table 3).

Table 3 Aggregation of field samples into analytical fractions (F1-F6) with the 3 variant setups (OTM-45, OTM-45 variant and cooled probe). The references of the field samples refer to the described treatment of the field samples above (§3.5).

FRACTIE	OTM-45	OTM-45 variant	Cooled probe
F1	Filter (S14) + Probe rinse + Front half rinse (S12)	Filter (S14) + Probe rinse + Front half rinse (S12)	Filter (S14) + Residu (S14*)
F2	Rinse condenser (S15) + rinse condensate flask (S19)	Rinse condenser (S15) + rinse condensate flask (S19)	Probe rinse (S12_1) + Rinse Condensate flasks (S19)
F3	Primary XAD-2 (S17)	Primary XAD-2 (S17)	Primary XAD-2 (S17)
F4	Condensate (S18) + water impingers (S20) + rinse impingers (S21)	Condensate (S18) + water impingers (S20) + rinse impingers (S21)	Condensate (S18) + Filtrate (S18*) + water impingers (S20) + rinse impingers (S21)
F5	Secondary XAD-2 (S22)	Secondary XAD-2 (S22)	Secondary XAD-2 (S22)
F6	Probe rinse cyclohex (S13) + Condenser rinse cyclohex (S16)	Probe rinse cyclohex (S13) + Condenser rinse cyclohex (S16)	Probe rinse cyclohex (S13)

3.6 PROCESSING ANALYTICAL FRACTIONS

The aggregated analytical fractions (Table 3) are further processed in the laboratory:

- The primary partial sample of this condensate is then combined with a partial sample of the water from the impingers (50/50). Internal standards are added to this mixed sample and the sample is extracted using solid phase extraction (SPE) as described further. The XAD-2 cartridge is extracted with alkaline methanol after removal of the water.
- The condenser rinse is combined with the condensate flask rinse (F2). Internal standards are added to this mixed sample and the sample is evaporated under a nitrogen stream.
- The front half rinse and probe rinse are used to extract the filter (F1).
- The rinsing liquid from the impingers is combined with the eluate from the SPE column after extraction of the water sample (F4).
- The secondary XAD-2 cartridge (F5) contains no water and is extracted as a separate sample with alkaline methanol.
- The cyclohexane rinses of the probe and condenser are combined (F6). Internal standards are added to this mixed sample and the sample is evaporated under a nitrogen stream.

3.7 TRANSPORT AND STORAGE

All field samples are transported on ice (4°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 long-chain (>C10) PFAS in water samples may decrease with increasing storage time, due to sorption on the container wall or precipitation (WAC/IV/A/025).

4 ANALYSIS PROCEDURE

The quantitative analysis of the analysis fractions is done in accordance with WAC/IV/A/025. The content of the various 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 MATERIAL EN REAGENTS

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

4.2 EXTRACTION FILTER (FRACTION F1)

- Transfer the filter to a (PP) tube.
- Add the probe rinse and and front half rinse, making sure the filter is completely submerged. Add additional alkaline methanol if necessary.
- Record the total volume of added liquid.
- 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 (IS) so that the theoretical concentration of the IS in the measurement extract is equal to that in the calibration standards.
- Vortex the whole thing for a few minutes.
- Sonicate for 1 hour, shaking every 15 minutes.
- Decant the solution into another (PP) tube.
- If necessary, evaporate the extract under a N2 stream to 500 µl; do not let the extract evaporate to dryness.
- If desired, dilute the extract with methanol or ultrapure water. The calibration standards must be prepared in the same solvent mixture as the measurement extracts.
- Transfer to a measuring vial
- The filter is extracted a second time with cyclohexane (complete immersion of the filter).
- Add an appropriate amount of the standard solution of internal standards (IS) so that the theoretical concentration of the IS in the measurement extract is equal to that in the calibration standards.
- The whole thing is vortexed for a few minutes
- Sonicate for 1 hour, shaking every 15 minutes.
- Decant the solution into another (PP) tube.
- Evaporate to dry under N_2 (cyclohexane is immiscible with ultrapure water or methanol).
- If desired, dilute the extract with methanol or ultrapure water. The calibration standards must be prepared in the same solvent mixture as the measurement extracts.
- Transfer to a measuring vial.

Typically 10 µl of the 2 extracts are 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 CONDENSER RINSE AND CONDENSATE FLASK RINSE (FRACTION 2)

- Combine the condenser rinse with the condensate flask rinse.
- 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.
- If necessary, evaporate the extract under a N2 stream to 500 µl; do not let the extract evaporate to dryness.
- If desired, dilute the extract with ultrapure water or methanol; the calibration standards must be prepared in the same solvent mixture as the measurement extracts.
- Transfer to a measuring vial.

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 XAD2 CARTRIDGES (FRACTION F3 AND F5)

- Before extraction, any water present in the XAD2 cartridge is purged under a N_2 flow. The drops of water from the cartridge are added to the condensate fraction (see §4.5 for the extraction).
- 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.
- Add 75 mL of the ammonia/methanol solution to the XAD-2 cartridge. The adsorbent must be completely immersed.
- Close the cartridge on both sides with glass caps.
- Shake the whole thing for a few minutes.
- Sonicate for 1 hour, shaking every 15 minutes.
- The glass caps are replaced by couplings and the extraction liquid is pushed out of the cartridge by means of a N_2 flow and collected in a PP tube.
- The cartridge is rinsed with 20 mL of methanol and combined with the 75 mL.
- If desired, the extract can be divided into 2 subfractions and one subfraction can be saved for reanalysis.
- If necessary, evaporate the entire extract under a N2 stream to 500 µl; do not let the extract evaporate to dryness.
- If desired, dilute the extract with ultrapure water or methanol; the calibration standards must be prepared in the same solvent mixture as the measurement extracts.
- Transfer to a measuring vial.

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 OF THE XAD2 WATER FRACTION, CONDENSATE AND IMPINGER WATER (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.
- Shake the mixture vigorously.
- An SPE-WAX cartridge is used for the extraction. The procedure includes the following steps:
    - condition the SPE cartridge with 4 ml ammonia/methanol solution;
    - condition the SPE cartridge with 4 ml of methanol;
    - rinse the SPE cartridge with 4 ml of ultrapure water; be careful not to let the pattern dry;
    - transfer the sub-sample (25 mL of the condensate with the water blown off from the XAD2 cartridge and 25 mL of water from the impingers, 50 mL) over the SPE cartridge;
    - rinse the sample bottle with 4 ml methanol and use it to elute the SPE cartridge; capture this fraction;
    - rinse the sample bottle with 4 ml methanol/ammonia solution and use it to elute the SPE cartridge; combine this fraction with the previous one;
    - Add the rinsing liquid from impinger 2,3,4 to the elution liquid;
- if necessary, evaporate the extract under a N2 stream to 500 µl; do not let the extract evaporate to dryness;
- if desired, dilute the extract with ultrapure water or methanol; the calibration standards must be prepared in the same solvent mixture as the measurement extracts;
- transfer to a measuring vial;

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 PROBE AND CONDENSER RINSES (FRACTION 6)

- Combine the probe cyclohexane rinse with the condenser cyclohexane rinse.
- 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.
- If necessary, evaporate the extract under a N_2 stream to 500 µl; do not let the extract evaporate to dryness.
- If desired, dilute the extract with ultrapure water or cyclohexane; the calibration standards must be prepared in the same solvent mixture as the measurement extracts.
- Transfer to a measuring vial.

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 carried out in accordance with WAC/IV/A/025.

5 REPORTING

The analysis 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 (<30%). The emission concentration ($C_{emission}$) of each compound (summed over the different analysis 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) must be applied in accordance with WAC/IV/A/025. The lower bound method is applied to each individual analysis fraction.

The sampled flow (V_samp) is calculated from the monitoring data of the gas counter, 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 sampled 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:

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

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 method. 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 XAD2 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 cylohexane rinses and the secondary XAD2 cartridge. The resulting analytical fractions (6) are delivered to the laboratory in an HDPE container:
    - S6: Probe rinse and front half rinse
    - S7: Glass wool or quartz fibre filter
    - S8: Condenser rinse
    - S9: XAD-2 (primary only)
    - S10: Impinger water
    - S11: Impinger rinse and condensate flask rinse

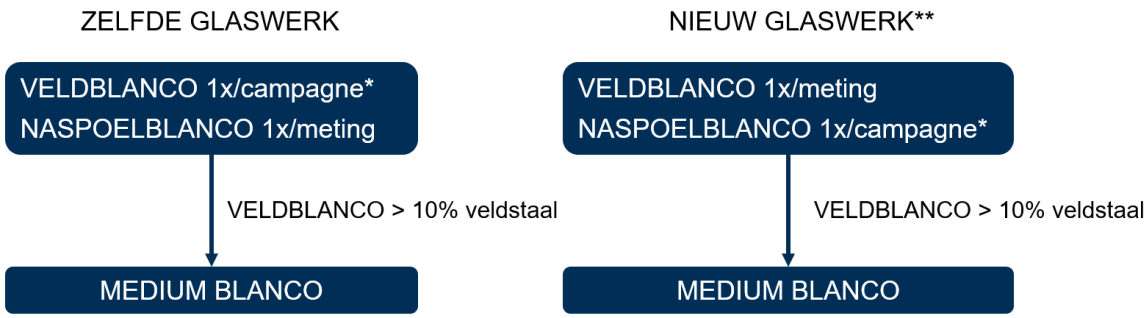
  The measured field blank concentrations in each fraction are also reported for interpretation of the analysis results.
- **Post-rinse blank (S23-S28 in Appendix 1):** After sampling and (3x) rinsing with alkaline methanol (methanol/1% NH4OH) and (3x) cyclohexane, the probe and filter holder (S23-24), condenser (S25-26), condensate flask and impingers are rinsed again 3 times with alkaline methanol and cyclohexane. The condensate flask (S27) and impingers (S28) are rinsed 3 times with methanol. The rinses are combined into 1 mixing sample per solvent (methanol/cyclohexane) and delivered to the laboratory in HDPE containers (1 methanol: S23 + S25 + S27 + S28 and 1 cyclohexane: S24 + S26). The purpose of the rinse blank is to check whether all PFAS have been adequately captured in the field sample (sampling + 3x rinsing).

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 the same 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 XAD2 to control for the entire sampling and analysis process. In this LUC method, both sampling standards for C8 (13C8-PFOA and 13C8-PFOS) and for C4 (13C3-PFBA) 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) XAD2 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
- Filter
- Uniquely engraved glassware + couplings (possibly with glass ball couplings):
- Condenser
- Condensation flask (1)
- Impingers (3)
- XAD2 cartridges (2), spiked with sampling standards (SS)
- Teflon lines (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 (§9.1) and 2 alternative sampling trains (§9.2) defined.

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 4.

Table 4 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 XAD2 cartridge	Sampling train variants (cooled probe, OTM-45 variant)
Analytical fractions (4): • filter + front half rinse • back half rinse + primary XAD2 • condensate + rinse condensate flask + impinger water + impinger rinse • secondary XAD-2	analytical fractions (6): • filter + front half rinse • primary XAD2 • 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-	Based on the observed blank concentrations, relaxation of blank collection frequency depening on the glassware use.

rinse blanks collected for every measurement	
Cooled XAD-2 cartridges	XAD2 cartridges are only cooled when temperature requirements (<20°C) cannot be fulfilled.
The OTM-45 method foresees A condensate flask and 3 additional impingers	minimum 1 condensate flask and 2 additional impingers in the sampling train
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 (XAD2) 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 XAD2 in original container, HDPE container with PP or PE lid or in glass container closed with glass lids.	Recovery XAD2 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 N_2 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)
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. This methodology was validated for 50 components.
QC/ REPORTING	
If the relative breakthrough is greater than 10%, the fraction of the 2nd XAD-2 is added	The 2nd XAD2 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.

to the sum of the other fractions and reported.	

8.2 SAMPLE TRAIN VARIANTS

8.2.1 OTM-45 VARIANT SAMPLE TRAIN

This sampling train includes the same measurement principle, compounds and sample preperation as the OTM-45 method (§2.1) but collects the condensate in a condensate flask before the gas flow is passed over the primary XAD2 cartridge (see the diagram below in Figure 2). After the primary XAD2 pattern, 3 impingers and a secondary XAD-2 pattern (breakthrough) are connected. The OTM-45 variant lineup includes:

- a heated probe with quartz filter
- a condenser
- an empty condensation bottle to collect the condensate
- a primary XAD2 pattern (beginning)
- a series of 3 impingers filled with ultrapure water
- a secondary XAD2 pattern (end)
- a drying tower (silica or equivalent desiccant) with pump

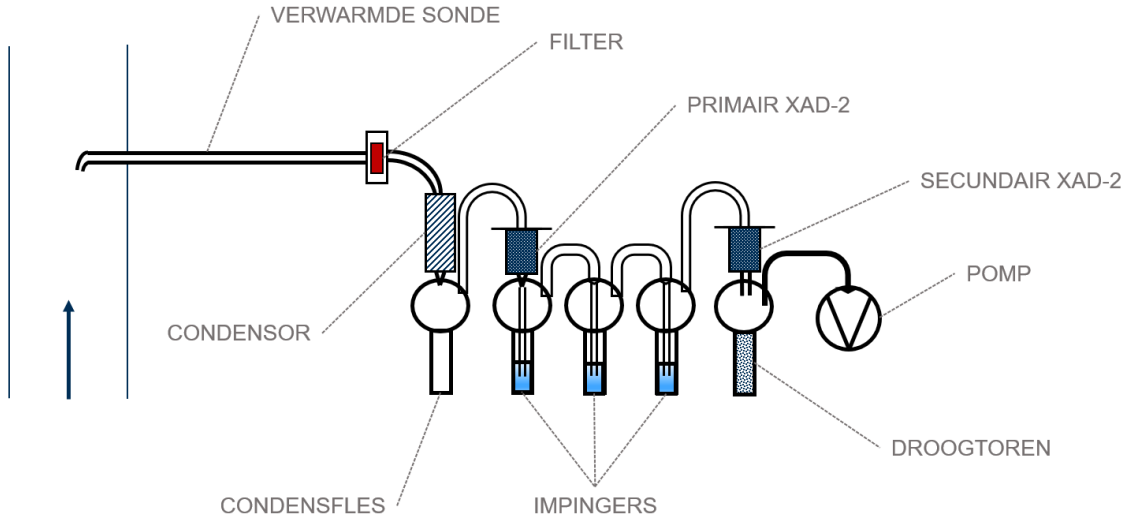


Figure 2 Schematic of the OTM-45 variant setup

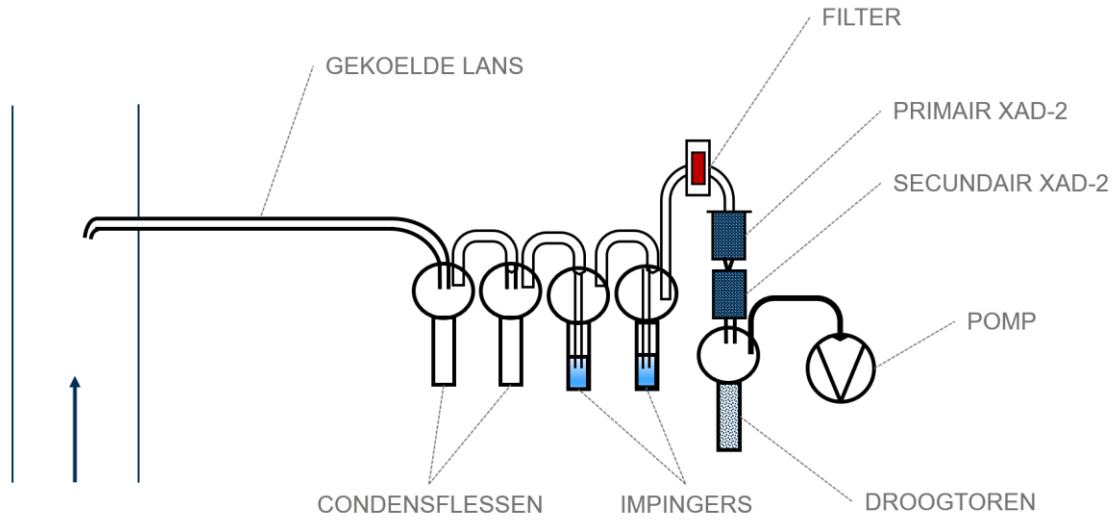
The sampling train mainly consists of borosilicate or quartz glass (probe, impingers, filter holder) and although Teflon (PTFE) should be avoided as much as possible (risk of contamination), it can possibly be used in connections, O-rings and/or coatings . Recovery of the samples takes place in existing cartridges (e.g. XAD2 cartridges), polypropylene (PP) or polyethylene (HDPE) bottles and results in 7 different samples (§3.5).

8.2.2 COOLED PROBE SAMPLING TRAIN

This sampling train provides isokinetic sampling by means of a cooled probe, followed by 2 condensate flasks (see the diagram below in Figure 3). The resulting dry gases then pass through a glass wool filter, a primary XAD2 cartridge, 2 impingers and a secondary XAD-2 cartridge. Any deposition of PFAS particles in the condensate is taken into account by an additional filtration. The

residue is added to the filter fraction and the filtrate to the condensate fraction. The cooled probe setup includes:

- a cooled probe
- 2 condensation flasks
- 2 impingers filled with ultrapure water
- a glass wool filter
- a primary XAD2 cartridge
- a secondary XAD2 cartridge
- a drying tower (silica or equivalent desiccant) with pump



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Figuur 3 Schematic of cooled probe sampling train

The sampling train mainly consists of borosilicate or quartz glass (probe, impingers, filter holder) and although Teflon (PTFE) should be avoided as much as possible (risk of contamination), it can possibly be used in connections, O-rings and/or coatings . Recovery of the samples takes place in existing cartridges (e.g. XAD2 cartridges), polypropylene (PP) or polyethylene (HDPE) bottles and results in 7 different samples (§3.5).

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

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 methanol
S3		Blank rinse cyclohexane
S4		blank XAD2
S5		blank water
S6	FIELD BLANC	Rinse probe – field blank
S7		filter- field blank
S8		Condenser rinse- field blank
S9		XAD2-1+spike - field blank
S10		impinger water - field blank
S11		impinger rinse - field blank
S12	SAMPLE	Probe rinse MeOH- Sample
S13		Probe rinse Cyclohex- Sample
S14		filter- Sample
S15		Condenser rinse MeOH - Sample
S16		Condenser rinse Cyclohex - Sample
S17		XAD2-1 + spike - Sample
S18		Condensate - Sample
S19		Condensate flask rinse- Sample
S20		impinger water- Sample
S21		impinger rinse - Sample
S22		XAD2-2 - Sample
S23	POST-RINSE BLANK	Probe rinse MeoH- post-rinse blank
S24		Probe rinse Cyclohex- post-rinse blank
S25		Condenser rinse MeoH- post-rinse blank
S26		Condenser rinse Cyclohex- post-rinse blank
S27		Condensate flask rinse MeoH- Sta post-rinse blank
S28		impinger rinse MeoH- post-rinse blank

Appendix 2: Applied sampling standards (SS)

		COMPOUND		STANDARD FOR
SS	SS1	Perfluoro-n-(13C8)octanoic acid (M8PFOA)	^{13}C8-PFOA	PFOA
	SS2	Sodium perfluoro-1-[13C8]octanesulfonate (M8PFOS)	^{13}C8-PFOS	PFOS
	SS3	Perfluoro-n-(2.3.4-13C3) butanoic acid (M3PFBA)	^{13}C3-PFBA	PFBA