

# PFAS: STAND VAN ZAKEN

DO Werkgroep Organische analyses 27/04/2021

## WAC-METHODE: INVLOED PH OP TERUGVINDING NA SPE

- Proefopzet: Evaluatie noodzaak pH aanpassing cfr ISO 21675 (pH 3)
  - 50 ml mineraalwater + 50 ng/l van elke PFAS
  - SPE extractie na pH aanpassing: pH 2, 5, 7, 9, 12
  
- Terugvindingen

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTTrDA	PFTeDA	PFHxDA	PFODA
pH2	101%	99%	99%	103%	100%	103%	101%	104%	102%	79%	102%	107%	-
pH5	98%	94%	96%	103%	98%	96%	97%	100%	105%	73%	98%	99%	-
pH7	95%	95%	96%	100%	96%	96%	98%	100%	97%	73%	97%	103%	-
pH9	98%	96%	99%	98%	98%	97%	99%	100%	100%	70%	105%	103%	-
pH12	101%	97%	97%	100%	97%	99%	101%	98%	102%	72%	109%	105%	-

	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFDoS	4:2 FTS	6:2 FTS	8:2 FTS	10:2 FTS
pH2	93%	102%	97%	93%	104%	83%	68%	40%	74%	101%	90%	80%
pH5	94%	101%	99%	91%	99%	80%	63%	35%	87%	100%	97%	69%
pH7	99%	99%	95%	84%	94%	78%	64%	38%	91%	103%	94%	75%
pH9	114%	110%	95%	79%	92%	79%	63%	37%	98%	101%	79%	50%
pH12	109%	107%	97%	82%	101%	79%	66%	41%	97%	104%	87%	60%

## WAC-METHODE: INVLOED PH OP TERUGVINDING NA SPE

	FOSA	MeFOSA	EtFOSA	MeFOSAA	EtFOSAA	6:2 diPAP	6:2/8:2 diPAP	8:2 diPAP	HFPO-DA	ADONA	PFECHS	9CI-PF3ONS	11CI-PF3OUdS
pH2	98%	105%	130%	100%	99%	103%	153%	101%	111%	111%	90%	79%	49%
pH5	97%	103%	111%	97%	90%	102%	101%	93%	102%	113%	70%	76%	50%
pH7	97%	98%	116%	94%	86%	97%	125%	98%	106%	102%	55%	70%	50%
pH9	98%	97%	102%	100%	86%	96%	73%	97%	106%	110%	47%	73%	54%
pH12	98%	100%	115%	100%	87%	95%	109%	101%	118%	117%	48%	72%	53%

### Terugvindingen IS

	13C-PFBA	13C-PFPeA	13C-PFHxA	13C-PFOA	13C-PFNA	13C-PFDA	13C-PUdA	13C-PFDoA	13C-PFTeDA	13C-PFHxDA
pH2	63%	59%	64%	70%	64%	62%	56%	47%	26%	29%
pH5	88%	78%	80%	85%	80%	74%	62%	44%	23%	63%
pH7	86%	76%	79%	84%	75%	69%	57%	45%	24%	33%
pH9	90%	84%	83%	79%	67%	53%	42%	40%	22%	22%
pH12	41%	77%	80%	77%	66%	56%	48%	35%	16%	28%

	13C-PFHxS	13C-PFOS	13C-6:2FTS	13C-FOSA	13C-MeFOSA	13C-MeFOSAA	13C-6:2 diPAP	13C-8:2 diPAP	13C-HFPO-DA
pH2	71%	57%	71%	70%	253%	58%	52%	286%	60%
pH5	73%	60%	77%	79%	240%	68%	43%	256%	72%
pH7	66%	49%	77%	78%	239%	67%	55%	296%	75%
pH9	57%	37%	79%	84%	252%	51%	31%	136%	74%
pH12	56%	38%	77%	74%	280%	51%	28%	231%	67%

### Conclusie: pH-aanpassing water is niet nodig

## WAC-METHODE: DEELSTAALNAME

- Proefopzet: Evaluatie deelmonstername
  - 25 ml mineraalwater geaddeerd met 50 ng/l PFAS (duplo)  
SPE opwerking volledig staal met naspoelen monsterfles
  - 200 ml + 50 ml MeOH, geaddeerd met 50 ng/l PFAS (duplo)  
SPE opwerking deelstaal 25 ml
  
- Terugvindingen

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTTrDA	PFTeDA	PFHxDA	PFODA
deelstaal1	98%	97%	99%	103%	95%	91%	81%	74%	61%	39%	61%	71%	-
deelstaal2	102%	100%	99%	107%	99%	93%	91%	77%	60%	35%	51%	62%	-
volledig staal1	101%	97%	101%	104%	102%	101%	102%	99%	102%	79%	101%	94%	-
volledig staal2	94%	94%	95%	100%	95%	94%	98%	94%	92%	63%	88%	96%	-

## WAC-METHODE: DEELSTAALNAME

	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFDoS	4:2 FTS	6:2 FTS	8:2 FTS	10:2 FTS
deelstaal1	100%	103%	95%	83%	85%	63%	38%	17%	94%	98%	76%	39%
deelstaal2	102%	105%	101%	88%	88%	64%	40%	16%	96%	108%	77%	39%
volledig staal1	94%	99%	100%	97%	85%	85%	73%	38%	92%	106%	112%	134%
volledig staal2	96%	98%	95%	86%	80%	71%	53%	26%	88%	100%	97%	101%

	FOSA	MeFOSA	EtFOSA	FOSAA	MeFOSAA	EtFOSAA	6:2 diPAP	6:2/8:2 diPAP	8:2 diPAP	HFPO-DA	ADONA	PFECHS	9CI-PF3ONS	11CI-PF3OUdS
deelstaal1	80%	58%	51%	0%	78%	66%	53%	90%	79%	105%	113%	56%	61%	27%
deelstaal2	80%	54%	53%	0%	83%	69%	55%	73%	81%	96%	106%	59%	61%	25%
volledig staal1	97%	95%	108%	0%	98%	98%	98%	83%	95%	118%	133%	68%	78%	53%
volledig staal2	92%	93%	99%	0%	96%	91%	94%	61%	95%	95%	99%	56%	65%	39%

- Conclusie: volledige opwerking monsterfles noodzakelijk

## WAC-METHODE: SPE WERKWIJZE

- Proefopzet: Evaluatie noodzaak spoelstap met NH<sub>4</sub>Ac buffer (cfr ISO) en centrifugatie
  - 25 ml effluent Stora Enso + 50 ng/l PFAS
  - SPE opwerking zonder en met NH<sub>4</sub>Ac spoelstap, resp. centrifugatiestap
  
- Terugvindingen

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTTrDA	PFTeDA	PFHxDA	PFODA
NH <sub>4</sub> Ac_centrifugeren_elueren	68%	81%	82%	109%	66%	93%	94%	103%	97%	89%	94%	95%	-
centrifugeren_elueren	76%	81%	85%	107%	70%	83%	96%	100%	93%	90%	88%	92%	-
NH <sub>4</sub> Ac_elueren	69%	87%	78%	105%	68%	85%	94%	100%	96%	74%	85%	92%	-
elueren	81%	98%	116%	121%	74%	94%	99%	102%	99%	87%	92%	92%	-

## WAC-METHODE: SPE

	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFDoS	4:2 FTS	6:2 FTS	8:2 FTS	10:2 FTS
NH4Ac_centrifugeren_elueren	78%	97%	96%	93%	80%	86%	87%	67%	71%	(1)	41%	34%
centrifugeren_elueren	86%	95%	95%	90%	79%	85%	86%	72%	68%	(1)	38%	30%
NH4Ac_elueren	81%	97%	96%	96%	77%	86%	81%	46%	69%	(1)	43%	31%
elueren	96%	103%	101%	93%	88%	90%	86%	73%	71%	(1)	37%	29%
	<i>(1) additie te laag tov oorspronkelijke waarde</i>											

	FOSA	MeFOSA	EtFOSA	MeFOSAA	EtFOSAA	6:2 diPAP	6:2/8:2 diPAP	8:2 diPAP	HFPO-DA	ADONA	PFECHS	9CI-PF3ONS	11CI-PF3OUdS
NH4Ac_centrifugeren_elueren	95%	97%	103%	98%	96%	105%	146%	90%	129%	134%	98%	84%	79%
centrifugeren_elueren	89%	95%	109%	92%	94%	89%	183%	82%	72%	90%	96%	83%	83%
NH4Ac_elueren	95%	98%	98%	92%	87%	88%	97%	84%	114%	109%	96%	84%	73%
elueren	99%	108%	117%	100%	102%	95%	174%	89%	112%	113%	103%	89%	82%

- Conclusie: spoelstap en centrifugatiestap kunnen weggelaten worden

## WAC-METHODE: HAALBARE LOQ

- Proefopzet: bepaling terugvindingen voor 1 ng/l resp. 5 ng/l waterstalen
  - Intake 50 ml (mineraalwater)
  - Uitvoering in triplicate
- Terugvindingen (*rood = afwijking 1 ng/l tov 5 ng/l*)

	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTTrDA	PFTeDA	PFHxDA	PFODA
LOQ1-1	195%	114%	120%	70%	110%	91%	83%	91%	138%	84%	43%	104%	-
LOQ1-2	198%	128%	107%	57%	123%	106%	87%	95%	121%	76%	68%	112%	-
LOQ1-3	211%	114%	114%	64%	122%	94%	84%	94%	117%	96%	59%	85%	-
Gemidd	201%	119%	114%	64%	118%	97%	85%	93%	125%	86%	57%	100%	-
RSD	4%	7%	6%	10%	6%	8%	3%	2%	9%	12%	22%	14%	-
LOQ5-1	105%	97%	102%	99%	100%	93%	99%	99%	100%	76%	87%	96%	-
LOQ5-2	123%	113%	106%	101%	108%	106%	102%	110%	101%	80%	95%	108%	-
LOQ5-3	126%	111%	109%	98%	113%	105%	111%	113%	111%	84%	92%	103%	-
Gemidd	118%	107%	105%	99%	107%	101%	104%	107%	104%	80%	91%	102%	-
RSD	9%	8%	3%	1%	6%	8%	6%	7%	6%	5%	5%	6%	-



## WAC-METHODE: HAALBARE LOQ

	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFDoS	4:2 FTS	6:2 FTS	8:2 FTS	10:2 FTS
LOQ1-1	155%	141%	103%	93%	138%	109%	54%	48%	73%	73%	68%	59%
LOQ1-2	159%	133%	105%	103%	137%	103%	54%	65%	70%	94%	84%	74%
LOQ1-3	150%	120%	99%	86%	131%	112%	47%	61%	64%	contaminatie	62%	68%
Gemidd	155%	131%	102%	94%	135%	108%	52%	58%	69%	83%	71%	67%
RSD	3%	8%	3%	9%	3%	4%	7%	16%	7%	18%	16%	11%
LOQ5-1	109%	105%	98%	90%	98%	87%	73%	55%	93%	98%	90%	76%
LOQ5-2	135%	116%	102%	95%	105%	93%	76%	57%	108%	110%	88%	72%
LOQ5-3	124%	120%	103%	95%	122%	101%	79%	60%	105%	114%	94%	77%
Gemidd	123%	114%	101%	93%	108%	93%	76%	58%	102%	108%	91%	75%
RSD	10%	7%	2%	3%	11%	8%	4%	4%	8%	8%	3%	3%

## WAC-METHODE: HAALBARE LOQ

	FOSA	MeFOSA	EtFOSA	MeFOSAA	EtFOSAA	6:2 diPAP	6:2/8:2 diPAP	8:2 diPAP	HFPO-DA	ADONA	PFECHS	9CI-PF3ONS	11CI-PF3OUdS
LOQ1-1	93%	125%	173%	115%	43%	101%	110%	183%	0%	91%	65%	115%	99%
LOQ1-2	95%	128%	159%	110%	55%	73%	100%	184%	0%	83%	67%	108%	100%
LOQ1-3	89%	128%	166%	104%	37%	88%	101%	160%	0%	79%	64%	104%	97%
Gemidd	92%	127%	166%	110%	45%	87%	104%	176%	0%	84%	65%	109%	99%
RSD	3%	2%	4%	5%	20%	16%	5%	8%	-	7%	3%	5%	2%
LOQ5-1	99%	98%	123%	94%	83%	97%	138%	96%	152%	105%	65%	83%	69%
LOQ5-2	111%	107%	130%	106%	90%	99%	142%	95%	69%	103%	58%	90%	76%
LOQ5-3	111%	112%	123%	109%	94%	108%	133%	106%	149%	120%	70%	98%	83%
Gemidd	107%	105%	125%	103%	89%	101%	138%	99%	123%	109%	64%	91%	76%
RSD	6%	7%	3%	8%	7%	6%	4%	6%	38%	8%	10%	8%	9%

- Conclusie: 1 ng/l is voor meeste PFAS haalbaar, voor andere is LOQ 1-5 ng/l

## TOPA (*Total oxidisable precursor assay*)

- Doel: detectie/kwantif. precursoren = non-target PFAS die potentieel kunnen afbreken tot target PFAS
- Alkalische oxidatie precursoren:
  - PFCAs, PFSAs: persistent
  - Telomeerverbindingen (FTSs, FTOHs, PAPs, ...) -> PFCAs
  - Sulfonamides (FOSAs, FOSAAs, FOSEs, FBSAs, ...) -> PFCAs, maar ook hydrolyse (PFOS, PFBS, ...)
  - PFECA's (HFPO-DA, ADONA, 9Cl-PF3ONS, ...) -> PFCAs indien niet geperfluoreerd
  - ...
- Eerste testen conform werkwijze *Houtz et al.* niet OK (onvoldoende afbraak precursoren, onvoldoende toename PFCAs)
- Uitvoering bijkomende testen:
  - 5 maal hogere dosering  $K_2S_2O_8$ , pH 13
  - Keuze recipient glas/PP
  - Betere controle temperatuur (waterbad ipv oven)
  - Roeren/schudden

## TOPA (*Total oxidisable precursor assay*)

- Werkwijze
  - 25 ml UP, additie PFAS 1 µg/l
  - Additie 2 g  $K_2S_2O_8$  en voeg 1.9 ml NaOH 10N toe, pH controleren, afsluiten
  - 6h laten reageren bij 85°C, schudden/roeren, pH controleren (pH≥12)
  - Neutraliseren met HCl 10N tot pH 5-8
  - 25 ml MeOH toevoegen, 5 min ultrasoon
  - Deelmonster 1 ml, additie IS en analyseer

## TOPA (*Total oxidisable precursor assay*)

- Keuze recipient: terugvindingen negatieve controle (1 µg/l, n = 3)

		<i>PFBA</i>	<i>PFPeA</i>	<i>PFHxA</i>	<i>PFHpA</i>	<i>PFOA</i>	<i>PFNA</i>	<i>PFDA</i>	<i>PFUdA</i>	<i>PFDoA</i>	<i>PFTrDA</i>	<i>PFTeDA</i>	<i>PFHxDA</i>	<i>PFODA</i>
<b>PP</b>	Recovery	139%	126%	126%	128%	127%	124%	117%	97%	83%	86%	78%	88%	100%
	RSD	9%	5%	3%	4%	7%	5%	8%	3%	8%	13%	9%	12%	39%
<b>GLAS</b>	Recovery	153%	112%	112%	116%	112%	114%	110%	109%	119%	122%	118%	117%	152%
	RSD	3%	4%	6%	4%	3%	3%	2%	6%	6%	7%	8%	15%	15%

		<i>PFBS</i>	<i>PFPeS</i>	<i>PFHxS</i>	<i>PFHpS</i>	<i>PFOS</i>	<i>PFNS</i>	<i>PFDS</i>	<i>PFDoS</i>	<i>4:2 FTS</i>	<i>6:2 FTS</i>	<i>8:2 FTS</i>	<i>10:2 FTS</i>
<b>PP</b>	Recovery	121%	124%	124%	124%	122%	114%	107%	104%	130%	166%	122%	104%
	RSD	4%	4%	3%	2%	6%	5%	4%	6%	3%	3%	5%	8%
<b>GLAS</b>	Recovery	109%	110%	113%	112%	111%	113%	116%	122%	112%	138%	117%	119%
	RSD	3%	6%	3%	6%	2%	1%	4%	6%	2%	13%	5%	0%

## TOPA (*Total oxidisable precursor assay*)

		<i>FOSA</i>	<i>MeFOSA</i>	<i>EtFOSA</i>	<i>MeFOSAA</i>	<i>EtFOSAA</i>	<i>6:2 diPAP</i>	<i>6:2/8:2 diPAP</i>	<i>8:2 diPAP</i>	<i>HFPO-DA</i>	<i>ADONA</i>	<i>PFECHS</i>	<i>9CI-PF3ONS</i>	<i>11CI-PF3OUdS</i>
<b>PP</b>	Recovery	62%	4%	3%	87%	68%	88%	74%	48%	109%	128%	131%	118%	103%
	RSD	8%	9%	17%	6%	6%	5%	6%	12%	11%	5%	5%	4%	6%
<b>GLAS</b>	Recovery	113%	93%	98%	113%	117%	121%	130%	106%	106%	115%	112%	112%	116%
	RSD	2%	17%	18%	2%	2%	12%	11%	11%	4%	7%	3%	1%	4%

- Conclusie: glas beter dan PP

## TOPA (*Total oxidisable precursor assay*)

- Additie UP water met 1 µg/l PFAS
- Vergelijking reactiecondities (n = 3)
  - WWB-S: Warmwaterbad, schudden, 6u, 85°C
  - WWB-R: Warmwaterbad, roeren, 6 u, 85°C (n =1 )
  - OV-US: Oven, elk uur tussentijds 5 min ultrasoniceren, 6 u, 85°C
  - OV-ZR: Oven, zonder roeren/ultrasoniceren, overnacht, 85°C

### ▪ Terugvindingen

		<i>PFBA</i>	<i>PFPeA</i>	<i>PFHxA</i>	<i>PFHpA</i>	<i>PFOA</i>	<i>PFNA</i>	<i>PFDA</i>	<i>PFUdA</i>	<i>PFDoA</i>	<i>PFTrDA</i>	<i>PFTeDA</i>	<i>PFHxDA</i>	<i>PFODA</i>
WWB-S	Recovery	146%	172%	218%	199%	497%	141%	121%	104%	101%	95%	103%	53%	21%
	RSD	8%	3%	3%	3%	4%	6%	4%	3%	13%	15%	9%	7%	23%
WWB-R	Recovery	287%	295%	298%	253%	421%	118%	72%	47%	38%	37%	36%	24%	12%
	RSD													
OV-US	Recovery	135%	149%	186%	128%	121%	21%	5%	4%	3%	3%	2%	3%	12%
	RSD	9%	7%	7%	2%	33%	32%	-	-	-	-	-	-	13%
OV-ZS	Recovery	136%	156%	196%	164%	407%	111%	104%	92%	92%	81%	82%	45%	16%
	RSD	7%	5%	4%	5%	5%	10%	18%	25%	26%	33%	34%	17%	4%

## TOPA (*Total oxidisable precursor assay*)

		<i>PFBS</i>	<i>PFPeS</i>	<i>PFHxS</i>	<i>PFHpS</i>	<i>PFOS</i>	<i>PFNS</i>	<i>PFDS</i>	<i>PFDoS</i>	<i>4:2 FTS</i>	<i>6:2 FTS</i>	<i>8:2 FTS</i>	<i>10:2 FTS</i>
WWB-S	Recovery	106%	106%	103%	105%	119%	106%	108%	103%	0%	1%	0%	0%
	RSD	6%	1%	1%	4%	3%	2%	6%	11%				
WWB-R	Recovery	125%	133%	133%	119%	119%	79%	69%	86%	0%	8%	0%	0%
	RSD												
OV-US	Recovery	110%	107%	75%	29%	20%	9%	8%	10%	0%	7%	0%	0%
	RSD	4%	6%	8%	36%	24%							
OV-ZS	Recovery	101%	102%	100%	99%	149%	94%	94%	88%	0%	0%	4%	11%
	RSD	5%	3%	2%	1%	7%	13%	12%	21%				

		<i>FOSA</i>	<i>MeFOSA</i>	<i>EtFOSA</i>	<i>FOSAA</i>	<i>MeFOSAA</i>	<i>EtFOSAA</i>	<i>6:2 PAP</i>	<i>8:2 PAP</i>	<i>6:2 diPAP</i>	<i>6:2/8:2 diPAP</i>	<i>8:2 diPAP</i>	<i>HFPO-DA</i>	<i>ADONA</i>	<i>PFECHS</i>	<i>9Cl-PF3ONS</i>	<i>11Cl-PF3OUds</i>
WWB-S	Recovery	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	103%	0%	101%	80%	80%
	RSD												5%		3%	9%	18%
WWB-R	Recovery	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	98%	0%	117%	35%	15%
	RSD																
OV-US	Recovery	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	92%	0%	45%	4%	3%
	RSD												7%		15%		
OV-ZS	Recovery	12%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	71%	51%	47%
	RSD														9%	5%	12%



## TOPA (*Total oxidisable precursor assay*)

	$\Sigma$ %afname precursors	$\Sigma$ %toename PFCA+PFOS
WWB-S	1339%	813%
WWB-R	1442%	1201%
OV-US	1486%	220%
OV-ZS	1474%	622%

### ■ Vaststellingen:

- Verhoogde C4-C9 PFCA conc.  
*Opm:* WWB-R en OV-US afname PFCA vanaf PFNA
- Constante PFSA conc, uitz. OV-ZS (toename PFOS) en OV-US (afname vanaf PFHxS)
- FTS, FOSAs, PAPs, ADONA kwantitatieve omzetting
- HFPO-DA persistent, uitz. OV-ZS
- 9Cl-PF3ONS en 11Cl-PF3OUdS: partiële omzetting

## TOPA (*Total oxidisable precursor assay*)

- Voorlopige conclusies:
  - goede controle T en roeren noodzakelijk
  - reële effluenten: invloed matrix op conversierendement
  - knelpunten: hoge zoutconc., SPE opconcentr. geen optie (vastlopen SPE kolom), hogere LOQ
  - verder onderzoek nodig om tot gestandaardiseerde werkwijze te komen

## AOF

- Bepaling totaal PFAS met CIC (*Combustion Ion Chromatography*)  
*zie ook nieuwe drinkwaterrichtlijn*  
*zie mogelijk totaal verbod PFAS in EU*
- DIN 38409-59 (ontwerp):
  - Waterstalen niet geconserveerd met HNO<sub>3</sub>
  - Adsorptie op actieve kool
  - Verbranding en captatie HF in absorptievloeistof
  - Bepaling F<sup>-</sup> met ionenchromatografie
- Best haalbare LOQ 2 µg/l
- Interlaboratoriumvalidatie DIN methode lopende

## PROEFRONDE PFAS - WAC/IV/A/025:2020

- Vooropgestelde timing: juni
- Stalen:
  - Drinkwater
  - Oppervlaktewater/grondwater
  - Afvalwaters (2)
- In combinatie met proefronde PFAS OVAM
  
- Opmerking: erkenningsronde in najaar (WAC/IV/A/025:2016)