Results of Proficiency Test Per-&Polyfluorinated Compounds in polymer, total September 2018

Organised by: Institute for Interlaboratory Studies
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1 INTRODUCTION

Perfluorooctanoic acid (PFOA) is one important representative of the substance group of per- and polyfluorinated substances. The hazard profile of PFOA is well known: PFOA is a persistent, bio-accumulative, and toxic substance, which may cause severe and irreversible adverse effects on the environment and human health. PFOA was the first PFC (Poly/Per Fluorinated Chemicals) to be identified as substance of very high concern (SVHC) under REACH by unanimous agreement between EU Member States in 2014. Besides PFOA also other fluorinated substances have properties of concern, which are targeted by the following international regulations: Perfluorinated carboxylic acids with a carbon chain of eleven to fourteen carbon atoms (PFBS, PFHxS, PFHxA, PFOS, PFNA, PFDA, 8:2 FTOH) are listed as SVHC on the REACH candidate list because of their persistent and bio-accumulative properties. Perfluoro-octane sulfonic acid (PFOS) is listed as persistent organic pollutant (POP) in Annex B of the Stockholm Convention.
To protect health and environment, the European Union promulgated Directive 2006/122/EC on 27 December 2006, in which the placing on the market and the use of per- and polyfluorinated substances is restricted: “Semi-finished products or articles, or parts thereof, if the concentration of PFOS/PFOA is equal or greater than 0.1% by mass” and “May not be placed on the market or used as a substance or constituent of preparations in a concentration equal to or higher than 0.005 % by mass.”

On request of several participants, the Institute for Interlaboratory Studies decided to organise an interlaboratory study for the determination of PFOA and PFOS content in the 2012 PT program. This PT was continued each following year. In this interlaboratory study 35 laboratories from 18 different countries registered for participation (See appendix 4). In this report, the results of the proficiency test are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

2 SET-UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organiser of this proficiency test. Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. It was decided to send 2 different plastic samples (approximately 3 grams each), artificially fortified on PFOS, PFOA and/or PFNA and labelled #18610 and #18611 respectively. Participants were requested to report rounded and unrounded test results and some details of the test methods used. The unrounded test results were preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in accordance with ISO/IEC 17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This PT falls under the accredited scope. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant’s data. Feedback from the participants on the reported data is encouraged and customer’s satisfaction is measured on regular basis by sending out questionnaires.

2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

Two different materials made of PVC were selected, sample #18610 artificially fortified to be positive on PFOS and sample #18611 artificially fortified on PFOA and PFNA. The materials were divided over 50 plastic bags, approx. 3 grams each. Sample #18610 consisted of light blue PVC squares and sample #18611 was white PVC rings.

The homogeneity of the subsamples of #18610 was checked by determination of PFOS content according to an in-house test method on eight stratified randomly selected subsamples of #18610.

	PFOS in mg/kg
sample #18610-1	681
sample #18610-2	697
sample #18610-3	697
sample #18610-4	698
sample #18610-5	682
sample #18610-6	671
sample #18610-7	702
sample #18610-8	683

Table 1: homogeneity test results of subsamples #18610

From the above test results the relative standard deviation was calculated and compared with 0.3 times the corresponding relative standard deviation of the reference method in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	PFOS (%)
RSD (observed)	1.6
Reference method	(iis PTs, see §4)
0.3 x RSD (reference method)	5.4

Table 2: evaluation of the relative standard deviation of subsamples #18610

The homogeneity of the subsamples of #18611 was checked by determination of PFOA and PFNA content according to an in-house test method on eight stratified randomly selected subsamples of #18611.

	PFOA in mg/kg	*PFNA in mg/kg*
sample #18611-1	406.6	465.0
sample #18611-2	385.7	453.6
sample #18611-3	379.7	443.3
sample #18611-4	401.3	456.6
sample #18611-5	419.0	478.1
sample #18611-6	389.7	461.3
sample #18611-7	371.9	429.4
sample #18611-8	384.5	439.4

Table 3: homogeneity test results of subsamples #18611

From the above test results the relative standard deviation was calculated and compared with 0.3 times the corresponding relative standard deviation of the reference method in agreement with the procedure of ISO 13528, Annex B2 in the next table:

	PFOA (%)	*PFNA (%)*
RSD_r (observed)	4.0	3.4
Reference method	(iis PTs, see §4)	(iis PTs, see §4)
0.3 x RSD (reference method)	5.4	5.4

Table 4: evaluation of the relative standard deviations of subsamples #18611

The calculated variation coefficient RSD for samples #18610 and #18611 were lower than 0.3 times the average PT uncertainties of previous PTs (see §4). Therefore, homogeneity of subsamples #18610 and #18611 was assumed.

To each of the participating laboratories 1 times sample #18610 and 1 times sample #18611 was sent on August 8, 2018.

2.5 ANALYSES

The participants were requested to determine on both samples the Total PFOA, Total PFOS, Total PFNA, Total PFDA and other Per- and Polyfluorinated substances. Also, some analytical details were requested to be reported.

It was explicitly requested to treat the samples as if they were routine samples and to report the test results using the indicated units on the report form and not to round the test results, but report as much significant figures as possible. It was also requested not to report ‘less than’ results which are above the detection limit, because such results can not be used for meaningful statistical calculations.

To get comparable test results, a detailed report form and a letter of instructions are prepared. On the report form, the reporting units are given as well as the reference test methods that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories are also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated per determination in appendix 1 of this report. The laboratories are presented by their code numbers.

Directly after the deadline, a reminder was sent to those laboratories that had not reported test results at that moment.
Shortly after the deadline, the available test results were screened for suspect data. A test result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the reported test results (no reanalysis). Additional or corrected test results are used for data analysis and the original reported test results placed under 'Remarks' in the result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report ‘’iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation’ of June 2018 (iis-protocol, version 3.5).

For the statistical evaluation, the unrounded (when available) figures were used instead of the rounded results. Test results reported as ‘<…’ or ‘>…” were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either ‘unknown’, ‘OK’, ‘suspect’ or ‘not OK’. After removal of outliers, this check was repeated. If a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

In accordance to ISO 5725 the original test results per determination were submitted subsequently to Dixon’s, Grubbs’ and or Rosner’s outlier tests. Outliers are marked by D(0.01) for the Dixon’s test, by G(0.01) or DG(0.01) for the Grubbs’ test and by R(0.01) for the Rosner’s test. Stragglers are marked by D(0.05) for the Dixon’s test, by G(0.05) or DG(0.05) for the Grubbs’ test and by R(0.05) for the Rosner’s test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. In this PT, the criterion of ISO13528, paragraph 9.2.1, was met for all evaluated tests, therefore the uncertainty of all assigned values may be negligible and need not be included in the PT report.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported analysis results are plotted. The corresponding laboratory numbers are on the X-axis.

The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected standard. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

Furthermore, Kernel Density Graphs were made. The Kernel Density Graph is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve was projected over the Kernel Density Graph for reference.

3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, the z-scores were calculated using a target standard deviation. This results in an evaluation, independent of the spread of this interlaboratory study.
The target standard deviation was calculated from the literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values were used. In some cases, a reproducibility of based on former iis proficiency tests could be used.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate whether the reported test result is fit-for-use.

The z-scores were calculated according to:

z(target) = (test result - average of PT) / target standard deviation

The z(target) scores are listed in the result tables of appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. Therefore, the usual interpretation of z-scores is as follows:

|z| < 1 good
1 < |z| < 2 satisfactory
2 < |z| < 3 questionable
3 < |z| unsatisfactory

4 EVALUATION

In this interlaboratory study, no problems were encountered with the dispatch of the sample. Three participants did not report any test result at all. Finally, the 32 reporting laboratories reported 118 numerical results. Observed was 1 outlying test result, which is 0.8%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

For the determination of PFOA/PFOS in textile, the CEN/TS 15968 method is considered to be the official EC test method by the majority of the participating laboratories. However, test method CEN/TS 15968 does not mention reproducibility requirements.
Up to now the calculated reproducibilities were compared with reproducibilities estimated from the Horwitz equation. Over the last two years an improvement is visible in the uncertainties of PFOA and PFOS (see table 6). However, it is doubtful whether the strict target reproducibility based on the Horwitz equation will ever be met. Therefore, it was decided to use a relative target reproducibility of 18% for this PT based on iis PT data of PFOA/PFOS proficiency tests from 2016 and 2017 (see also paragraph 5).

Also, no official test method exists for the determination of PFNA. It was decided to use for the evaluation of PFNA the same target reproducibility of 18% as described for PFOA and PFOS in this PT.

All original data sets proved to have a normal Gaussian distribution.

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this paragraph, the test results are discussed per sample and per component.

Test method Test CEN/TS 15968 chapter 8 it is stated that for polymers and granulates it is recommended to use ISO 6427. In ISO 6427 (table 1 and 2) a number of extraction methods is listed dependent on type of polymers. It is recommended to use Soxhlet for PVC. Therefore, the test results from participants that did not use Soxhlet for extraction were excluded from the statistical evaluations (see also appendix 1).

Sample #18610:

PFOS: Severe analytical problems were observed in determining the PFOS concentration at a level of 513 mg/kg. The reported PFOS concentration varies over a large range from 120 to 3930 mg/kg. One statistical outlier was observed and twenty test results were excluded from statistical evaluation. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility found in previous iis PTs.

For PFOA, PFNA, PFDA and other Per- Polyfluorinated substances the majority of the participants agreed on a concentration near or below the limit of detection. The material had not been spiked with these components. Therefore, it was decided not to calculate z-scores for these determinations.

Sample #18611

PFOA: Severe analytical problems were observed in determining the PFOA concentration at a level of 383 mg/kg. The reported PFOA concentration varies over a large range from 2.7 to 547 mg/kg. No statistical outliers were observed, but twenty test results were excluded from statistical evaluation. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility found in previous iis PTs

PFNA: Severe analytical problems were observed in determining the PFNA concentration at a level of 352 mg/kg. The reported PFNA concentration varies over a large range from 4.3 to 548 mg/kg. No statistical outliers were observed, but sixteen test results were excluded from statistical evaluation. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility found in previous iis PTs for PFOA/PFOS.

For PFOS, PFDA and other Per- Polyfluorinated substances the majority of the participants agreed on a concentration near or below the limit of detection. The material had not been spiked with these components. Therefore, it was decided not to calculate z-scores for these determinations.

4.2 PERFORMANCE EVALUATION OF THE GROUP OF LABORATORIES

The calculated reproducibilities and the target reproducibilities estimated from previous PT's, are compared in below table.

	unit	n	average	2.8 * sd	R(iis-PTs)
PFOS in #18610	mg/kg	11	513	308	240
PFOA in #18611	mg/kg	12	383	227	204
PFNA in #18611	mg/kg	7	352	340	187

Table 5: performance overview for the test results on samples #18610 and #18611

Without further statistical calculations, it can be concluded that there is no good compliance of the group of participating laboratories with the target reproducibilities.

4.3 COMPARISON OF PROFICIENCY TEST OF SEPTEMBER 2018 AGAINST PREVIOUS PTS

The observed variation expressed as the relative standard deviation RSD of the test results in the 2018 PT is almost the same with the observations in previous PTs, see below table.

	2018	*2017*	*2016 *)*	*2015 -2014 *)*	*iis Target*	*Target Horwitz 100-2000 mg/kg*
PFOS	22%	13-24%	11-19%[a]	24[s] - 128%[a]	18%	9 - 14% **)
PFOA	21%	20%	18%	144%	18%	7 - 11% **)
PFNA	34%	n.d.	n.d.	n.d.	18%	9% **)

Table 6: development of uncertainties, reported as RSD, over **all (a**) or over **subset (s)** of results against previous PTs.

*) See respective published PT reports on www.iisnl.com for the explanation about the subsets

**) Horwitz estimation based on 2 isomers for PFOA and PFNA and 3 isomers for PFOS

For PFOA/PFNA/PFOS the target value for the precision of the PFOA, PFNA and PFOS content determination in polymers was based on the PT results from previous PTs (2016 and 2017).

4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this proficiency test some analytical details were requested, see appendix 3. Based on the answers given by the participants the following can be summarized:
23 of the 31 reporting participants (=74%) mentioned that they are accredited for determination of Per & Polyfluorinated Compounds in polymers
Twenty-one participants mentioned that they have further cut/grinded the samples before use and ten participants mentioned to have used the samples as received.
Most participants (61%) used ultrasonic technique to release/extract the analytes, while 39% of the participants mentioned to have used Soxhlet as extraction technique.

All participants mentioned to have used Methanol in combination with or without Dichloromethane or Toluene as extraction solvent, except one who use THF.
The participants that used Soxhlet extraction used an extraction time of 6 hrs, while the extraction time used by Ultrasonic was 2 hrs or less.

5 DISCUSSION

The CEN/TS 15968 method is very comprehensive in the description of the analytical part after the sample pre-treatment and quite brief about the sample pre-treatment and extraction from polymers. This description about sample pre-treatment is mainly the extraction from materials such as paper or textile by ultrasonic bath in Methanol for 2h at 60°C. And 32% of the participants reported to use this pre-treatment. For the reduction of solid polymers by grinding, the CEN/TS 15968 method refers to EN ISO 6427 and to ISO 9113 for a list of extractions conditions dependent on a type of polymer.

The evaluation of Per- and Polyfluorinated Compounds in polymer in sample #18610 and sample #18611 was problematic for about two-third of the reporting laboratories.
Twenty test results for PFOS in sample #18610, twenty test results for PFOA and sixteen test results for PFNA in sample #18611 were excluded from the statistical evaluation to get a good estimation of the consensus value of the components which were added to the polymers (see paragraph 2).
It is observed that the variation is dependent on the chosen sample pre-treatment and extraction procedure, see table 7 and 8. In general, more PFOS and PFOA is determined when the material is cut and/or Soxhlet extraction technique is used.

Analytical Details	*unit*	*n*	*average*	*2.8 * sd*	*RSD (%)*
Ultrasonic extraction	mg/kg	18	355	468	47
Soxhlet distillation	mg/kg	11	512	308	21

Table 7: reproducibility of PFOS in polymer sample #18610

Analytical Details	*unit*	*n*	*average*	*2.8 * sd*	*RSD (%)*
Ultrasonic extraction	mg/kg	19	89	294	118
Soxhlet distillation	mg/kg	12	383	226	21

Table 8: reproducibility of PFOA in polymer sample #18611

Obviously, the determination of Per- and Polyfluorinated Compounds becomes more consistent when sample pre- treatment release PFOA and PFOS more effectively from the polymer.

6 CONCLUSION

The conclusion is that many of the participants has some difficulty to determine Per- and Polyfluorinated Compounds in polymer matrix. The variation is dependent on the chosen sample pre-treatment and extraction procedure.
Each laboratory should evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

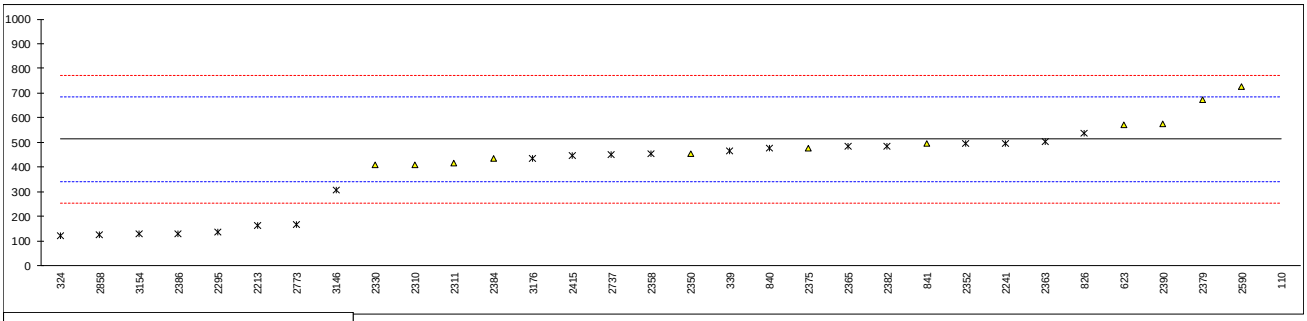
APPENDIX 1

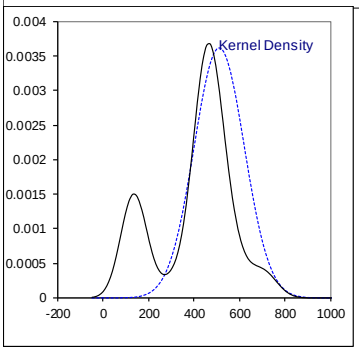
Determination of PFOS on sample #18610; results in mg/kg

lab	method	value	mark	z(targ)	Remarks
110	In house	3930.227	R(0.01)	37.03	
324	In house	120	ex	-4.26	
339	In house	463.80	ex	-0.53	
623	CEN-TS15968	571.63		0.64	
826	CEN-TS15968	535.916	ex	0.25	
840	In house	477	ex	-0.39	
841	CEN-TS15968	494.94		-0.19	
2213	CEN-TS15968	161.82	C, ex	-3.80	First reported 14.25
2241	CEN-TS15968	496.6	ex	-0.18	
2295	CEN-TS15968	137	C, ex	-4.07	First reported 13.7
2310	CEN-TS15968	410		-1.11	
2311	CEN-TS15968	414.8		-1.06	
2330	CEN-TS15968	407.75	C	-1.14	First reported 746.22
2350	In house	452.99		-0.65	
2352	CEN-TS15968	495.2	ex	-0.19	
2358	CEN-TS15968	452.35	C, ex	-0.65	First reported 152.35
2363	CEN-TS15968	504	ex	-0.10	
2365	CEN-TS15968	483.3	ex	-0.32	
2375	CEN-TS15968	477.3		-0.38	
2379	CEN-TS15968	671.63		1.72	
2382	CEN-TS15968	484.9	ex	-0.30	
2384	CEN-TS15968	435.51	C	-0.84	First reported 862.88
2386	CEN-TS15968	130.976	ex	-4.14	
2390	CEN-TS15968	576.13		0.69	
2410		-----		-----	
2415	In house	445.1	ex	-0.73	
2590	CEN-TS15968	727.92079		2.33	
2737	CEN-TS15968	450.78	ex	-0.67	
2773	In house	166	C, ex	-3.76	First reported 14.25
2858	In house	123.88	C, ex	-4.21	First reported 93.26
3146	CEN-TS15968	305.4	ex	-2.25	
3154	CEN-TS15968	129.60	ex	-4.15	
3163		-----		-----	
3176	In house	436.60	ex	-0.83	
3210		-----		-----	

	normality	OK	
	n	11	
	outliers	1 (+20excl)	
	mean (n)	512.782	
	st.dev. (n)	110.1422	
	R(calc.)	308.398	
	st.dev.(iis)	92.3007	
	R(iis)	258.442	
Compare			
	R(Horwitz)	155.556	(3 components)

ex= test result excluded, see paragraph 4.1



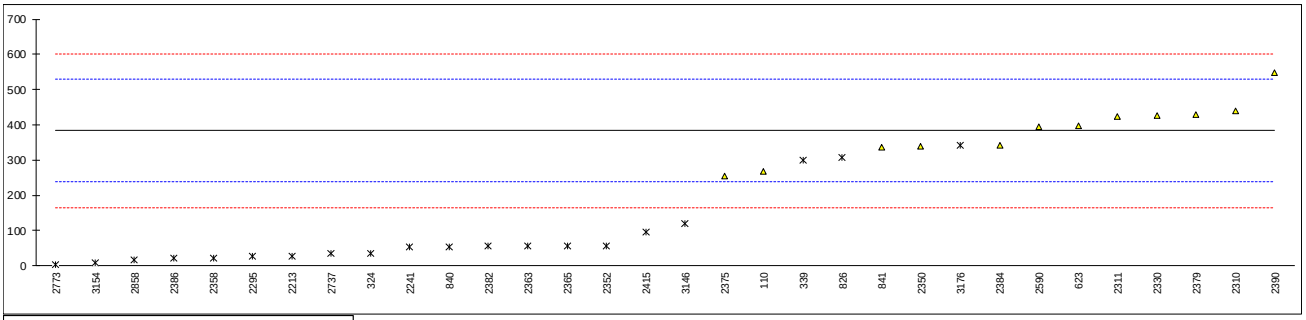


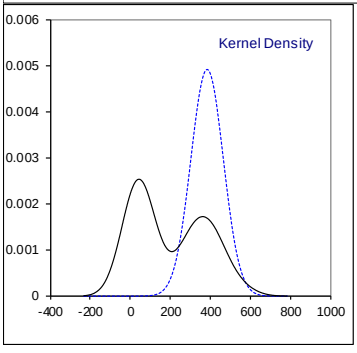
Determination of PFOA on sample #18611; results in mg/kg

lab	method	value	mark	z(targ)	Remarks
110	In house	266.499		-1.69	
324	In house	36	ex	-5.03	
339	In house	299.53	ex	-1.21	
623	CEN-TS15968	396.72		0.20	
826	CEN-TS15968	308.179	ex	-1.09	
840	In house	54.2	ex	-4.77	
841	CEN-TS15968	337.265		-0.67	
2213	CEN-TS15968	28	C, ex	-5.15	First reported 2.8
2241	CEN-TS15968	53.1	ex	-4.79	
2295	CEN-TS15968	28	C, ex	-5.15	First reported 2.8
2310	CEN-TS15968	440		0.82	
2311	CEN-TS15968	424.8		0.60	
2330	CEN-TS15968	426.36		0.63	
2350	In house	338.29		-0.65	
2352	CEN-TS15968	57.3	ex	-4.72	
2358	CEN-TS15968	20.65	ex	-5.26	
2363	CEN-TS15968	55	ex	-4.76	
2365	CEN-TS15968	56.6	ex	-4.73	
2375	CEN-TS15968	254.4		-1.87	
2379	CEN-TS15968	429.39		0.67	
2382	CEN-TS15968	54.8	ex	-4.76	
2384	CEN-TS15968	342.67		-0.59	
2386	CEN-TS15968	20.520	ex	-5.26	
2390	CEN-TS15968	546.95		2.37	
2410		-----		-----	
2415	In house	97.0	ex	-4.15	
2590	CEN-TS15968	395.12100		0.17	
2737	CEN-TS15968	34.29	ex	-5.06	
2773	In house	2.7	ex	-5.52	
2858	In house	16.91	ex	-5.31	
3146	CEN-TS15968	120.5	ex	-3.81	
3154	CEN-TS15968	8.42	ex	-5.43	
3163		-----		-----	
3176	In house	341.70	ex	-0.60	
3210		-----		-----	

	normality	OK	
	n	12	
	outliers	0 (+20 excl)	
	mean (n)	383.205	
	st.dev. (n)	80.9434	
	R(calc.)	226.642	
	st.dev.(iis)	68.9770	
	R(iis)	193.136	
Compare			
	R(Horwitz)	99.170	(2 components)

ex= test result excluded, see paragraph 4.1



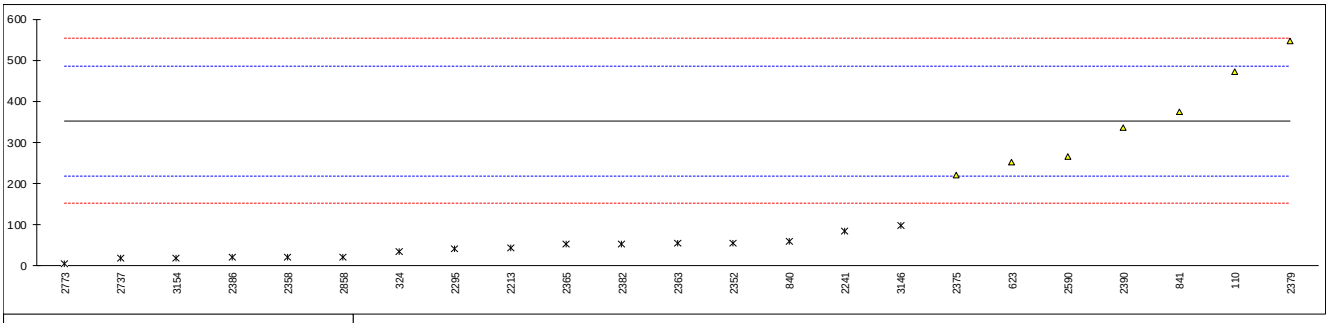


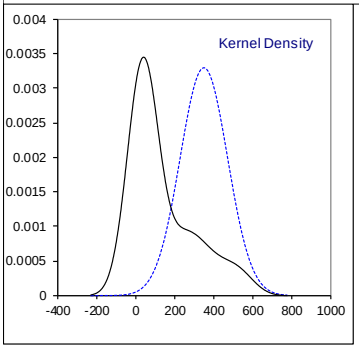
Determination of PFNA on sample #18611; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	471.530		1.88	
324	In house	34	ex	-5.02	
339		-----		-----	
623	CEN-TS15968	252.44		-1.58	
826		-----		-----	
840	In house	60.5	ex	-4.60	
841	CEN-TS15968	373.977		0.34	
2213	CEN-TS15968	44	Cex	-4.86	First reported 4.3
2241	CEN-TS15968	83.8	ex	-4.23	
2295	CEN-TS15968	41	Cex	-4.91	First reported 4.1
2310		-----	W	-----	Test result withdrawn, reported 375
2311		-----		-----	
2330		-----		-----	
2350	In house	N/A		-----	
2352	CEN-TS15968	54.7	ex	-4.69	
2358	CEN-TS15968	20.91	ex	-5.23	
2363	CEN-TS15968	54	ex	-4.70	
2365	CEN-TS15968	52.5	ex	-4.73	
2375	CEN-TS15968	220	C	-2.09	First reported 313.8
2379	CEN-TS15968	547.78		3.08	
2382	EPA3540C/8321B	52.9	ex	-4.72	
2384		-----		-----	
2386	CEN-TS15968	20.803	ex	-5.23	
2390	CEN-TS15968	336.1	C	-0.26	First reported 580.62
2410		-----		-----	
2415		-----		-----	
2590	CEN-TS15968	264.7	C	-1.38	First reported 415.242
2737	CEN-TS15968	18.26	ex	-5.27	
2773	In house	4.3	ex	-5.49	
2858	In house	20.97	ex	-5.22	
3146	CEN-TS15968	98.5	ex	-4.00	
3154	CEN-TS15968	19.31	ex	-5.25	
3163		-----		-----	
3176		-----		-----	
3210		-----		-----	

	normality	OK	
	n	7	
	outliers	0 (+16excl)	
	mean (n)	352.361	
	st.dev. (n)	121.3189	
	R(calc.)	339.693	
	st.dev.(iis)	63.4250	
	R(iis)	177.590	
compare			
	R(Horwitz)	92.347	(2 components)

ex= test result excluded, see paragraph 4.1





APPENDIX 2 Other reported test results

Determination of PFOA, PFNA and PFDA on sample #18610; results in mg/kg

lab	method	PFOA	PFNA	PFDA
110	In house	2.561	ND	ND
324	In house	0.038	0	0
339		0.351	-----	-----
623	CEN-TS15968	n.d.	n.d.	n.d.
826		-----	-----	-----
840	In house	n.d.	n.d.	n.d.
841	CEN-TS15968	ND	ND	ND
2213	CEN-TS15968	<1	<1	<1
2241		-----	-----	-----
2295		-----	-----	-----
2310	CEN-TS15968	0.201	NOT DETECTED	NOT DETECTED
2311		0.299	-----	-----
2330		ND	-----	-----
2350	In house	<1.00	N/A	<1.00
2352		-----	-----	-----
2358	CEN-TS15968	n.d.	n.d.	n.d.
2363	CEN-TS15968	<1	<1	<1
2365	CEN-TS15968	<1.0	<1.0	<1.0
2375		-----	-----	-----
2379	CEN-TS15968	Not detected	Not detected	Not detected
2382		-----	-----	-----
2384		Not detected [<10]	-----	-----
2386		0.113	-----	-----
2390	CEN-TS15968	ND	ND	ND
2410		-----	-----	-----
2415		-----	-----	-----
2590		0.37461	-----	-----
2737	CEN-TS15968	0.20	ND	ND
2773	In house	<1.0	<1.0	<1.0
2858	In house	n.d	n.d	n.d
3146	CEN-TS15968	0.788	<0.1	<0.1
3154		-----	-----	-----
3163		-----	-----	-----
3176		0.17	-----	-----
3210		-----	-----	-----

Lab 110 Possibly a false positive test result?

Determination of Other Per- and Polyfluorinated substances on sample #18610; results in mg/kg

lab	method	Other Per- and Poly	comments
110	EPA3540C/8321B	4043.7	
324	Other	3.116	Other per- and polyfluorinated substances = PFBS, PFHxA, PFHxS, PFHpA, PFPA, PFBA and PFPeA. All concentrations include both linear and branched isomers of the different PFCs.
339		-----	Method : LC/MS/MS
623	CEN-TS15968	n.d.	
826		-----	
840		-----	
841	CEN-TS15968	as Comments	PFHxS: 59.821 mg/kg PFHpS: 26.457 mg/kg
2213	CEN-TS15968	<1	
2241		-----	
2295		-----	
2310	CEN-TS15968	as Comments	PFHxS = 56.9 mg/kg ,PFHpS = 20.7mg/kg and PFHxA = 0.285 mg/kg
2311		-----	
2330		-----	
2350	Other	N/A	In house method
2352		-----	
2358	CEN-TS15968	49.12	
2363	CEN-TS15968	<1	
2365		-----	
2375		-----	PFHxS = 75 mg/kg PFHpS = 32 mg/kg
2379		-----	
2382		-----	
2384		-----	
2386	CEN-TS15968	30.665	
2390		-----	
2410		-----	
2415		-----	
2590		-----	We also found others PFCs: PFBA = 0.416 mg/kg PFPA = 0.384 mg/kg PFHxA = 0.388 mg/kg PFHpA = 0.316 mg/kg PFHxS = 67.604 mg/kg PFHpS = 25.382 mg/kg
2737	CEN-TS15968	ND	
2773	Other	<1.0	
2858	Other	10.49	PFHxS = 10.49 mg/kg
3146		-----	
3154		-----	
3163		-----	
3176		-----	
3210		-----	

Lab 110 Possibly a false positive test result?

Determination of PFOS and PFDA on sample #18611; results in mg/kg

lab	method	PFOS	PFDA
110	In house	2.356	ND
324	In house	0.015	0
339	In house	0.161	-----
623	CEN-TS15968	n.d.	n.d.
826		-----	-----
840	In house	n.d.	n.d.
841	CEN-TS15968	ND	ND
2213	CEN-TS15968	<1	<1
2241		-----	-----
2295		-----	-----
2310	CEN-TS15968	0.210	NOT DETECTED
2311	CEN-TS15968	0.199	-----
2330	CEN-TS15968	ND	-----
2350	In house	<1.00	<1.00
2352		-----	-----
2358	CEN-TS15968	n.d.	n.d.
2363	CEN-TS15968	<1	<1
2365	CEN-TS15968	<1.0	<1.0
2375		-----	-----
2379	CEN-TS15968	Not detected	Not detected
2382		-----	-----
2384	CEN-TS15968	Not detected [<10]	-----
2386	CEN-TS15968	0.019	-----
2390	CEN-TS15968	ND	ND
2410		-----	-----
2415		-----	-----
2590	CEN-TS15968	0.10316	-----
2737	CEN-TS15968	0.07	ND
2773	In house	<1.0	<1.0
2858	In house	n.d	n.d
3146	CEN-TS15968	0.691	-----
3154		-----	-----
3163		-----	-----
3176	In house	0.06	-----
3210		-----	-----

Determination of Other Per- and Polyfluorinated substances on sample #18611; results in mg/kg

lab	method	Other Per- and Poly	comments
110	In house	3089.7	
324	In house	0.432	Other per- and polyfluorinated substances = PFHxA, PFHpA and PFBA. All concentrations include both linear and branched isomers of the different PFCs.
339		-----	Method : LC/MS/MS
623	CEN-TS15968	n.d.	
826		-----	
840	In house	-----	
841	CEN-TS15968	as Comments	PFHpA: 4.578mg/kg
2213	CEN-TS15968	<1	
2241		-----	
2295		-----	
2310	CEN-TS15968	as Comments	PFHxA = 0.625 mg/kg
2311		-----	
2330		-----	
2350	In house	N/A	In house method
2352		-----	
2358	CEN-TS15968	n.d.	
2363	CEN-TS15968	<1	
2365	CEN-TS15968	-----	
2375		-----	
2379	CEN-TS15968	-----	
2382		-----	
2384		-----	
2386		0.623	
2390	CEN-TS15968	-----	
2410		-----	
2415		-----	
2590		-----	We also found others PFCs compound not listed above: PFBA = 0.879 mg/kg PFHxA = 0.800 mg/kg PFHpA = 6.051 mg/kg
2737	CEN-TS15968	ND	
2773	In house	<1.0	
2858	In house	n.d	In-house test method followed.
3146		-----	
3154		-----	
3163		-----	
3176		-----	
3210		-----	

Lab 110 Possibly a false positive test result?

APPENDIX 3 Analytical details

lab	Accredited acc. ISO /IEC17025 for this test?	Sample used as received or further grinded/cut	Used to release/extract the analyte(s)	Solvent (mixture) to release the analyte(s)	Extraction time (minutes)	Extraction temperature (°C)
110	Yes	Further Cut	Soxhlet	MeOH:DCM 1:1	360 minutes	Boiling
324	Yes	Used as received	Mechanical Shaking	Methanol	2 hours	Room T
339	No	Further Cut	Ultrasonic	Methanol / Toluene	120	60
623	No	Further Cut	Soxhlet	Methanol/ DCM	6 hours	
826	No	Further Grinded	Ultrasonic	Methanol	120min	60
840	Yes	Further Cut	Ultrasonic	methanol	120	60
841	No	Further Cut	Soxhlet	Methanol/ DCM (1:1)	360	
2213	Yes	Further Cut	Ultrasonic			
2241	Yes	Further Cut	Ultrasonic	methanol	2 hours	60°C
2295	Yes	Used as received	Ultrasonic	Methanol	120	60
2310	Yes	Used as received	Soxhlet	DCM:Methanol(1:1)	6 hours	70°C
2311	Yes	Further Cut	Soxhlet	DCM and Methanol	360 minutes	80
2330	No	Further Cut	Soxhlet	MeOH: DCM (1:1)	360 min	60°C
2350	No	Used as received	Soxhlet	Methanol	6 hours	50°C
2352	Yes	Further Cut	Ultrasonic	methanol	120min	60°C
2358	Yes	Used as received	Ultrasonic	Methanol	120 min	60 degree C
2363	Yes	Further Cut	Ultrasonic	Methonal	2h	60°C
2365	Yes	Further Cut	Ultrasonic	Methanol	120 min	60°C
2375	Yes	Further Cut	Soxhlet	Methanol : DCM (1:1)	90 mins	105 C
2379	No	Further Cut	Soxhlet	DCM:MeOH (1:1)	360	100
2382	No	Further Cut	Ultrasonic	Methanol	120min	60°C
2384	Yes	Further Grinded	Soxhlet	methanol : DCM (1:1)	6 hours	under reflux T
2386	Yes	Used as received	Ultrasonic	MeOH	120	60
2390	Yes	Further Cut	Soxhlet	MeOH: DCM 1:1	6 hours	
2410	---	---	---			
2415	Yes	Further Cut	Ultrasonic	THF	120	60
2590	Yes	Further Cut	Soxhlet	MEOH/DCM 1:1	360	Not applicable
2737	Yes	Used as received	Ultrasonic	methanol	120min	60°C
2773	---	---	---			
2858	Yes	Used as received	Ultrasonic	Methanol	60 Minutes	60
3146	Yes	Further Grinded	Ultrasonic	MeOH	120min	60°C
3154	Yes	Used as received	Ultrasonic			
3163	---	---	---			
3176	Yes	Used as received	Ultrasonic	DCM/MeOH	120 min	60°C
3210	---	---	---			

APPENDIX 4

Number of participants per country:

1 lab in BANGLADESH
1 lab in BELGIUM
1 lab in CAMBODIA
2 labs in FRANCE
3 labs in GERMANY
1 lab in HONG KONG
4 labs in INDIA
1 lab in INDONESIA
1 lab in ITALY
3 labs in KOREA
1 lab in MALAYSIA
6 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in THAILAND
1 lab in THE NETHERLANDS
3 labs in TURKEY
1 lab in U.S.A.
3 labs in VIETNAM

APPENDIX 5

Abbreviations

C = final test result after checking of first reported suspect test result
D(0.01) = outlier in Dixon's outlier test
D(0.05) = straggler in Dixon's outlier test
G(0.01) = outlier in Grubbs' outlier test
G(0.05) = straggler in Grubbs' outlier test
DG(0.01) = outlier in Double Grubbs' outlier test
DG(0.05) = straggler in Double Grubbs' outlier test
R(0.01) = outlier in Rosner's outlier test
R(0.05) = straggler in Rosner's outlier test
W = test result withdrawn on request of participant
ex = test result excluded from statistical evaluation
n.a. = not applicable
n.e. = not evaluated
n.d. = not detected

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