Results of Proficiency Test Per-&Polyfluorinated Compounds in Textile March 2020

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Perfluorooctanoic acid (PFOA) is one important representative of the substance group of per- and polyfluorinated substances (PFAS). The hazard profile of PFOA is well-known: PFOA is a persistent, bioaccumulative, and toxic substance, which may cause severe and irreversible adverse effects on the environment and human health. PFOA has a harmonized classification in Annex VI of European Regulation (EC) No. 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP – Classification, Labelling, Packaging) as Carcinogenicity (Carc.2), Reproductive toxicity (Repr.1B) and Specific Target Organ Toxicity (STOT RE 1 (liver)). Total PFOA and its ammonium salt (APFO) have been identified as substances of very high concern (SVHC) under REACH by unanimous agreement between EU Member States in 2014.
Another well-known PFAS is Perfluorooctanesulfonic acid (PFOS) and shall not be used as a substance or constituent in preparations of products with a concentration equal to or higher than 0.005 % by mass (50 mg/kg). Otherwise, products will be restricted to be placed on the market (Limits outlined by EU REACH (Directive 1907/2006/EC)) and OEKO-TEX®. Limits for the concentration of PFOS in textiles or other coated materials is set on equal or higher than 1 µg/m^2. Perfluorooctanoic acid (PFOA) and its salts are suspected to have a similar risk profile as to PFOS. Another article (see lit 19) showed that textiles could be a significant direct and indirect source of PFOS and PFOA exposure for both humans and the environment.

Since 2017 the Institute for Interlaboratory Studies organizes a proficiency scheme for the determination of Per-&Polyfluorinated Compounds in textile every year. During the annual proficiency testing program 2019/2020, it was decided to continue the proficiency test for the analysis of Per-&Polyfluorinated Compounds in textile.
In this interlaboratory study 65 laboratories from 19 different countries registered for participation. See appendix 4 for the number of participants per country. In this report, the results of this 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 organizer of this proficiency test. Sample analyzes for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory. It was decided to send 2 different textile samples positive on PFOA or PFOS of 5 grams each and labelled #20535 and #20536 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 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC17043:2010. 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 organization 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

For the first sample a batch of orange cotton was selected which was made positive on PFOA by a third-party. A part of this batch was cut into small pieces. After homogenization the batch was divided over 70 subsamples in small bags of approximately 5 grams each and labelled #20535. The homogeneity of the subsamples was checked by determination of total PFOA using an in-house test method on eight stratified randomly selected subsamples.

	Total PFOA in mg/kg
Sample #20535-1	7.13
Sample #20535-2	7.37
Sample #20535-3	7.59
Sample #20535-4	7.74
Sample #20535-5	7.47
Sample #20535-6	7.34
Sample #20535-7	7.04
Sample #20535-8	7.30

Table 1: homogeneity test results of subsamples #20535

From the above test results the repeatability was calculated and compared with 0.3 times the estimated reproducibility of the reference method in agreement with the procedure of ISO13528, Annex B2 in next table.

	Total PFOA in mg/kg
r (observed)	0.64
reference method	Horwitz (n=2)
0.3 * R (reference method)	1.04

Table 2: evaluation of the repeatability of subsamples #20535

The calculated repeatability was in agreement with the 0.3 times estimated reproducibility calculated using the Horwitz equation. Therefore, homogeneity of the subsamples was assumed.

For the second sample a batch of beige cotton was selected which was made positive on PFOS by a third-party. A part of this batch was cut into small pieces. After homogenization the batch was divided over 70 subsamples in small bags of approximately 5 grams each and labelled #20536. The homogeneity of the subsamples was checked by determination of total PFOS using an in-house test method on eight stratified randomly selected subsamples.

	Total PFOS in mg/kg
Sample #20536-1	6.62
Sample #20536-2	7.08
Sample #20536-3	6.97
Sample #20536-4	6.67
Sample #20536-5	6.98
Sample #20536-6	7.34
Sample #20536-7	6.73
Sample #20536-8	6.81

Table 3: homogeneity test results of subsamples #20536

From the above test results the repeatability was calculated and compared with 0.3 times the estimated reproducibility of the reference method in agreement with the procedure of ISO13528, Annex B2 in next table.

	Total PFOS in mg/kg
r (observed)	0.67
reference method	Horwitz (n=3)
0.3 * R (reference method)	1.20

Table 4: evaluation of the repeatability of subsamples #20536

The calculated repeatability was in agreement with 0.3 times the estimated reproducibility calculated using the Horwitz equation. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample #20535 and one sample #20536 of 5 grams each were sent on February 12, 2020.

2.5 ANALYZES

The participants were asked to determine on samples #20535 and #20536: Perfluorooctanoic acid (Total PFOA), Perfluorooctanesulfonic acid (Total PFOS), Perfluorononanoic acid (Total PFNA), Perfluorodecanoic acid (Total PFDA), Perfluorobutanesulfonic acid (Total PFBS) and ”other” per-&polyfluorinated substances. It was requested to report if the laboratory was accredited for the requested components that were determined and to report some analytical details. It was noted in the instructions of this PT to use no less than 0.5 grams per determination to ensure the homogeneity.

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 to report as much significant figures as possible. It was also requested not report ‘less than’ results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluations.

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 appropriate 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 were 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.iisn.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 and 2 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 original test results are placed under 'Remarks' in the test 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 organization of this proficiency test was the one as described for proficiency testing in the report ‘iis Interlaboratory Studies: Protocol for the Organization, 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 test 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 dataset does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

According to ISO5725 the original test results per determination were submitted 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 these with a factor of 2.8.

3.2 GRAPHICS

In order to visualize 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 test 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 reference test method. 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. This 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 variation 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 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 test result tables in 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

During the execution of this proficiency test no problems occurred with the dispatch of the samples. However, four laboratories informed iis that they were not able to report test results due to the measures taken to contain the Covid-19 pandemic in their country. Finally, three participants did not report any test results. The 62 reporting laboratories reported 123 numerical results. Observed were 7 outlying test results, which is 5.7%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or “suspect”. The statistical evaluation of these data sets should be used with due care, see also paragraph 3.1.

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this section, the reported test results are discussed per sample and per component. The test methods, which were reported by the laboratories were taken into account for explaining the observed differences when possible and applicable. These test methods are also in the table together with the original data. The abbreviations, used in these tables, are explained in appendix 5.

For the determination of Per- and Polyfluorinated compounds in textile, the CEN-TS 15968 method may be considered to be the official EC test method. Regretfully, the CEN-TS 15968 method does not mention reproducibility requirements. Therefore, the target requirements in this study were estimated using the Horwitz equation based on two or three components, see paragraph 5.

Please note that by the term “Total” is meant the sum of linear and branched isomers (see paragraph 5).

Sample #20535

Total PFOA: This determination was problematic. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility calculated using the Horwitz equation (2 components).

For other Per- and Polyfluorinated compounds, the majority of the participants agreed on a concentration near or below the limit of detection. Therefore, no z-scores were calculated for these substances. The reported test values are given in appendix 2.

Sample #20536

Total PFOS: This determination was not problematic. Three statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outliers is in agreement with the estimated reproducibility calculated using the Horwitz equation (3 components).

For other Per- and Polyfluorinated compounds, the majority of the participants agreed on a concentration near or below the limit of detection. Therefore, no z-scores were calculated for these substances. The reported test values are given in appendix 2.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the estimated target reproducibility using the Horwitz equation and the reproducibility as found for the group of participating laboratories. The number of significant test results, the average, the calculated reproducibility (2.8 * standard deviation) and the estimated reproducibility are presented in the next tables.

Component	unit	n	average	2.8 * sd	R(target)
Total PFOA	mg/kg	57	5.43	3.57	2.67

Table 5: performance overview for sample #20535

Component	unit	n	average	2.8 * sd	R(target)
Total PFOS	mg/kg	59	6.72	3.32	3.91

Table 6: performance overview for sample #20536

Without further statistical calculations, it can be concluded that the group of participating laboratories have some problems with the analysis of Total PFOA in textile. See also the discussion in paragraphs 4.1 and 5.

4.3 COMPARISON OF PROFICIENCY TEST OF MARCH 2020 WITH PREVIOUS PTS.

	March 2020	March 2019	March 2018	March 2017
Number of reporting laboratories	62	54	49	72
Number of test results	123	189	132	263
Number of statistical outliers	7	5	8	17
Percentage of statistical outliers	5.7%	2.6%	6.1%	6.5%

Table 7: comparison with previous proficiency tests

In proficiency tests, outlier percentages of 3% - 7.5% are quite normal.

The observed variation expressed as relative standard deviation RSD over the test results is compared to the relative target standard deviation, see below table.

Component	March 2020	March 2019	March 2018	March 2017	Target Horwitz (0.5 - 10 mg/kg)
Total PFOA	23%	22% - 24%	18%	18% - 31%	25% - 16%
Total PFOS	18%	25% - 33%	11%	15% - 27%	31% - 20%
Total PFDA	n.e.	19%	n.e.	n.e.	31% - 20%

Table 8: development of uncertainties (RSD) over the years

The target value for the precision of the Total PFOA or Total PFOS determination in textile is based on the Horwitz equation (respectively based on 2 or 3 components).

4.4 EVALUATION OF THE ANALYTICAL DETAILS

In this PT, also some analytical details were asked (see appendix 3) to use for further statistical analysis.
Around 74% of the participants mentioned to be accredited for the determination of Per-&Polyfluorinated substances in textile.
About 70% of the reporting participants mentioned to use test method CEN/TS 15968 for the determination of Total PFOA/Total PFOS. About 20% of the participants reported to have used in house method and 10% of the reporting participants used a different test method.
All participants used the Ultrasonic technique to release/extract the analyte, except for seven participants that did not report the technique used.
Remarkably, the amount of sample used for the determination was less than the test method described. Test method CEN/TS 15968 mentions to use 2 g. About 75% of the participants reported to use an intake of 1.5 gram or less. Unfortunately, the number of data is too limited for an in-depth analysis of the sample intake on the performances.

When evaluating the above differences in the execution of the test on the compounds determined, no clear correlation was found between these test conditions and the reported test result.

5 DISCUSSION

In legislation and in the limits set for PFOS/PFOA it is clear that **total** PFOS and **total** PFOA is meant. However, in the available test methods this is less clear. Test method CEN/TS 15968 mentions the existence of linear and branched isomers and the possibility to separate these isomers. Also, it is mentioned that branched isomers should be based on the response factor of the linear isomer. But method CEN/TS 15968 is not clear whether the sum of linear and branched isomers should be reported.

For most laboratories, it is not clear whether the sum or the linear isomer is determined. Therefore, it was decided not to ask for linear and branched isomers in this proficiency test, but only the sum of linear and branched isomers. Therefore, the term “total” was used.

In the 2017 PT on PFOA/PFOS in textile (iis17A05) it became clear that both components have branched and linear isomers. And in the 2017 PT more data were collected over the amount of linear, branched and total PFOA/PFOS. Next to this data also the chromatograms were collected from the participating laboratories. Based on the chromatograms the Horwitz equation was calculated based on 2 components for PFOA (in general two peaks were visible in the chromatograms) and on 3 components for PFOS (in general three peaks were visible).

When the results of this interlaboratory study were compared to the OEKO-TEX® requirements and Bluesign® regulations on Textiles (table 9), it is noticed that all of the reporting laboratories would reject sample #20535 and #20536 for containing too much Total PFOA or Total PFOS.

	OEKO-TEX®	Bluesign® BSSL v6.0
Total PFOA	<1.0 µg/m^2	<1.0 µg/m^2 (corresponds with <0.01 mg/kg)
Total PFOS	<1.0 µg/m^2	<1.0 µg/m^2 (corresponds with <0.01 mg/kg)
Total PFDA	<0.05, <0.1, <0.5 mg/kg (different categories)	<0.05 mg/kg

Table 9: Ecolabelling Standards for Textiles in EU

Sample #20535 was also used in a previous proficiency test iis18A02 as sample #18516. The obtained PT results are in line with the previous PT (see table 10).

Component	unit	Sample #20535			Sample #18516		
		n	average	2.8 * sd	n	average	2.8 * sd
PFOA	mg/kg	57	5.43	3.57	30	5.53	2.78

Table 10: comparison sample #18516 vs #20535

6 CONCLUSION

In the PT of 2020, the majority of the laboratories identified the added PFOA in sample #20535 and PFOS in sample #20536 correctly.

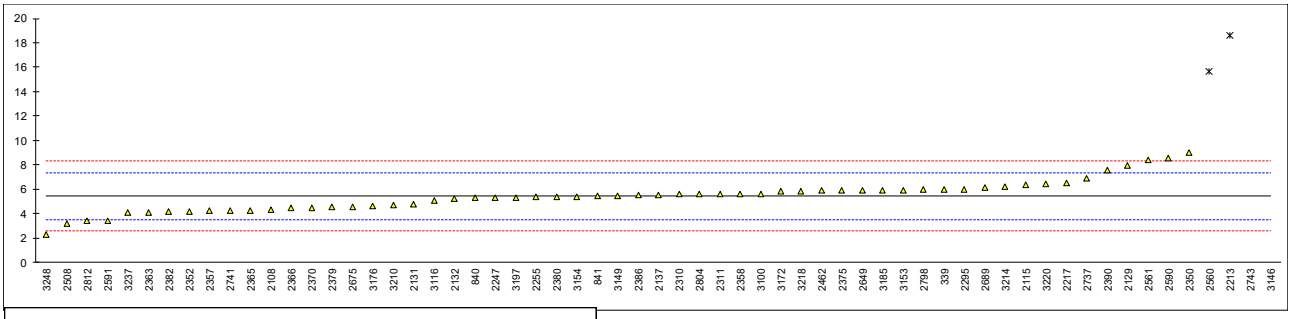
The variations observed in this interlaboratory study can be caused by the preparation or the conditioning of the sample and/or by the performance of the analysis by the participating laboratory. Consequently, the reproducibility cannot be improved by only one change in the analysis. Each laboratory has to 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 thus increase of the quality of the analytical results.

APPENDIX 1

Determination of Total PFOA on sample #20535; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	5.99		0.59	
840	CEN-TS15968	5.3		-0.14	
841	CEN-TS15968	5.48		0.05	
2108	In house	4.314		-1.17	
2115	CEN-TS15968	6.385		1.00	
2129	CEN-TS15968	7.912		2.60	
2131	In house	4.7652343		-0.70	
2132	In house	5.198		-0.25	
2137	KS M9722	5.50		0.07	
2213	ISO23702-1	18.6	R(0.01)	13.82	
2217	CEN-TS15968	6.5313		1.15	
2247	CEN-TS15968	5.31		-0.13	
2255	CEN-TS15968	5.37		-0.06	
2295	CEN-TS15968	6.0	C	0.60	First reported 18
2310	CEN-TS15968	5.59		0.17	
2311	CEN-TS15968	5.598		0.17	
2350	CEN-TS15968	8.97		3.71	
2352	CEN-TS15968	4.15		-1.35	
2357	CEN-TS15968	4.253		-1.24	
2358	CEN-TS15968	5.604		0.18	
2363	CEN-TS15968	4.110		-1.39	
2365	CEN-TS15968	4.27		-1.22	
2366	CEN-TS15968	4.44		-1.04	
2370	CEN-TS15968	4.51		-0.97	
2375	CEN-TS15968	5.9		0.49	
2379	CEN-TS15968	4.58		-0.89	
2380	CEN-TS15968	5.4		-0.03	
2382	CEN-TS15968	4.15		-1.35	
2386	CEN-TS15968	5.49787		0.07	
2390	CEN-TS15968	7.54		2.21	
2462	EPA3550C/8321B	5.88		0.47	
2508	DIN38414	3.1756		-2.37	
2560	CEN-TS15968	15.63	R(0.01)	10.70	
2561	In house	8.3800		3.09	
2590	CEN-TS15968	8.5850		3.31	
2591	In house	3.44		-2.09	
2649	In house	5.9		0.49	
2675	CEN-TS15968	4.585		-0.89	
2689	EPA3540C/8321B	6.10		0.70	
2737	CEN-TS15968	6.8912		1.53	
2741	CEN-TS15968	4.254		-1.24	
2743	CEN-TS15968	51.9626	C,R(0.01)	48.84	First reported 23.6205
2798	CEN-TS15968	5.96		0.55	
2804	In house	5.59		0.17	
2812	CEN-TS15968	3.4		-2.13	
2886		-----		-----	
2912		-----		-----	
3100	CEN-TS15968	5.607		0.18	
3116	CEN-TS15968	5.101		-0.35	
3118		-----		-----	
3146	In house	5313	R(0.01)	5571.10	Possibly a unit error?
3149	CEN-TS15968	5.48		0.05	
3153	CEN-TS15968	5.91		0.50	
3154		5.404		-0.03	
3172		5.831		0.42	
3176	CEN-TS15968	4.65		-0.82	
3185	CEN-TS15968	5.90		0.49	
3197	CEN-TS15968	5.32		-0.12	
3200		-----		-----	
3210	In house	4.723		-0.74	
3214	CEN-TS15968	6.234		0.84	
3218	CEN-TS15968	5.84		0.43	
3220	CEN-TS15968	6.47		1.09	
3237	CEN-TS15968	4.1		-1.40	
3248	In house	2.28		-3.31	

normality	suspect	
n	57	
outliers	4	
mean (n)	5.4317	
st.dev. (n)	1.27471	RSD = 23%
R(calc.)	3.5692	
st.dev.(Horwitz 2 comp)	0.95270	
R(Horwitz 2 comp)	2.6676	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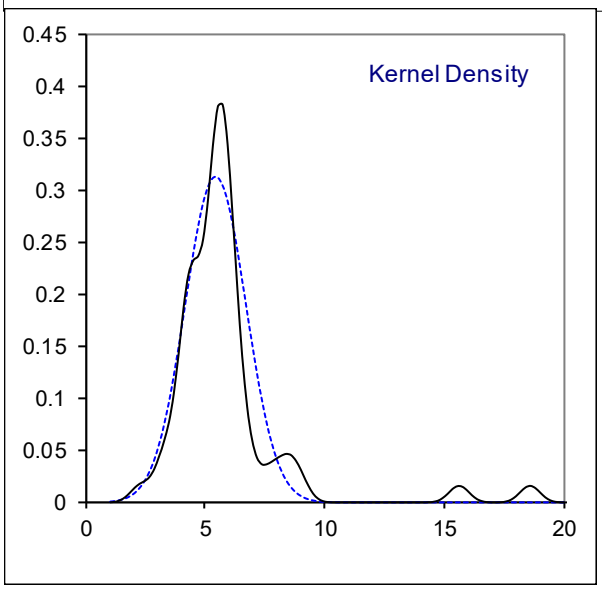
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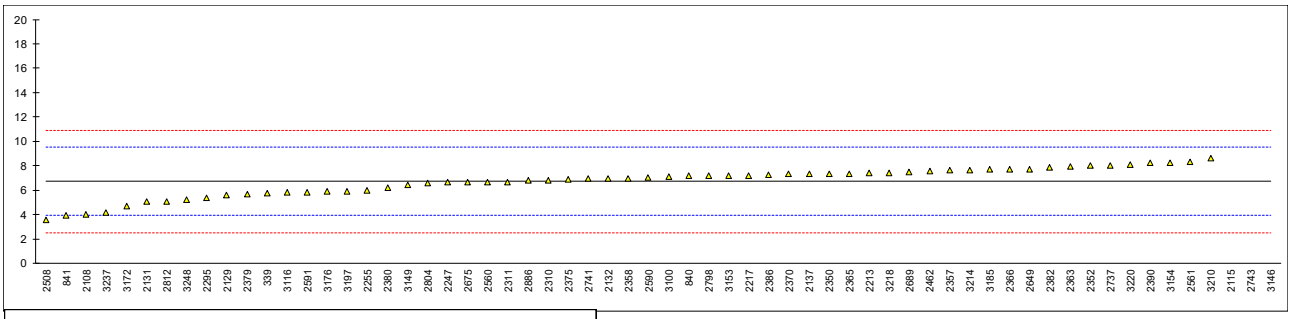
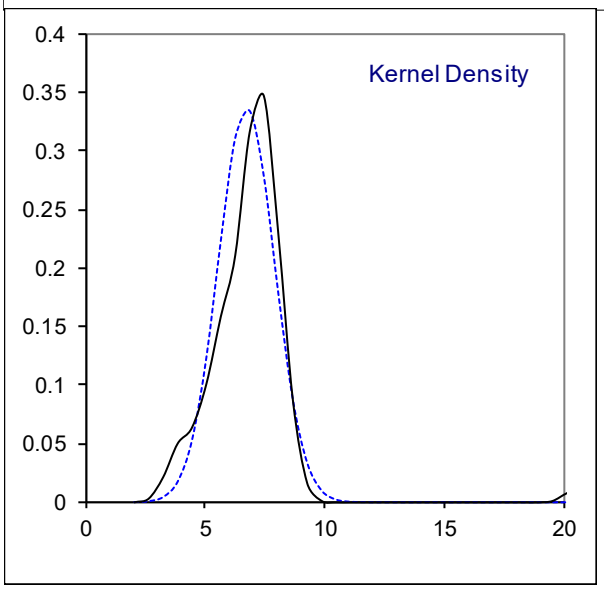
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20

Determination of Total PFOS on sample #20536; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	5.73		-0.71	
840	CEN-TS15968	7.2		0.34	
841	CEN-TS15968	3.93		-2.00	
2108	In house	4.041		-1.92	
2115	CEN-TS15968	20.624	R(0.01)	9.95	
2129	CEN-TS15968	5.575		-0.82	
2131	In house	5.0524564		-1.19	
2132	In house	6.959		0.17	
2137	KS M9722	7.318		0.43	
2213	ISO23702-1	7.4		0.49	
2217	CEN-TS15968	7.21956		0.36	
2247	CEN-TS15968	6.63		-0.06	
2255	CEN-TS15968	5.97		-0.54	
2295	CEN-TS15968	5.4	C	-0.94	First reported 7.5
2310	CEN-TS15968	6.84		0.09	
2311	CEN-TS15968	6.697		-0.02	
2350	CEN-TS15968	7.32		0.43	
2352	CEN-TS15968	8.02		0.93	
2357	CEN-TS15968	7.620		0.64	
2358	CEN-TS15968	6.968		0.18	
2363	CEN-TS15968	7.962		0.89	
2365	CEN-TS15968	7.35		0.45	
2366	CEN-TS15968	7.73		0.72	
2370	CEN-TS15968	7.31		0.42	
2375	CEN-TS15968	6.9		0.13	
2379	CEN-TS15968	5.68		-0.74	
2380	CEN-TS15968	6.2		-0.37	
2382	CEN-TS15968	7.90		0.85	
2386	CEN-TS15968	7.26534		0.39	
2390	CEN-TS15968	8.23		1.08	
2462	EPA3550C/8321B	7.56		0.60	
2508	DIN38414	3.5610		-2.26	
2560	CEN-TS15968	6.68		-0.03	
2561	In house	8.335		1.16	
2590	CEN-TS15968	7.0610		0.24	
2591	In house	5.83		-0.64	
2649	In house	7.7592563		0.74	
2675	CEN-TS15968	6.640		-0.06	
2689	EPA3540C/8321B	7.50		0.56	
2737	CEN-TS15968	8.0403		0.95	
2741	CEN-TS15968	6.951		0.17	
2743	CEN-TS15968	154.2996	C,R(0.01)	105.58	First reported 45.5307
2798	CEN-TS15968	7.21		0.35	
2804	In house	6.56		-0.11	
2812	CEN-TS15968	5.1		-1.16	
2886	In house	6.8104		0.07	
2912		-----		-----	
3100	CEN-TS15968	7.124		0.29	
3116	CEN-TS15968	5.828		-0.64	
3118		-----		-----	
3146	In house	5319	R(0.01)	3800.40	Possibly a unit error?
3149	CEN-TS15968	6.40		-0.23	
3153	CEN-TS15968	7.21		0.35	
3154		8.251		1.10	
3172		4.720		-1.43	
3176	CEN-TS15968	5.91		-0.58	
3185	CEN-TS15968	7.69		0.69	
3197	CEN-TS15968	5.93		-0.56	
3200		-----		-----	
3210	In house	8.656		1.39	
3214	CEN-TS15968	7.684		0.69	
3218	CEN-TS15968	7.44		0.52	
3220	CEN-TS15968	8.11		1.00	
3237	CEN-TS15968	4.2		-1.80	
3248	In house	5.24		-1.06	
	normality	OK			
	n	59			
	outliers	3			
	mean (n)	6.7188			
	st.dev. (n)	1.18489	RSD = 18%		
	R(calc.)	3.3177			
	st.dev.(Horwitz 3 comp)	1.39782			
	R(Horwitz 3 comp)	3.9139			


20
18
16
14
12
10
8
6
4
2
0
2508 841 2108 3237 3172 2131 2812 3248 2295 2129 2379 339 3116 2691 3176 3197 2255 2380 3149 2804 2247 2675 2560 2311 2886 2310 2375 2741 2132 2368 2590 3100 840 2798 3153 2217 2386 2370 2137 2350 2365 2213 3218 2689 2462 2357 3214 3185 2366 2649 2382 2363 2362 2737 3220 2390 3154 2561 3210 2115 2743 3146


Kernel Density
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20

APPENDIX 2: **Other reported test results**

Determination of Total PFOS, Total PFNA, Total PFDA, Total PFBS and other Per-and Polyfluorinated substances on sample #20535; in mg/kg

lab	Total PFOS	Total PFNA	Total PFDA	Total PFBS	Other Per and Polyfluorinated substances
339	<0.1	-----	<0.1	-----	-----
840	n.d.	n.d.	n.d.	n.d.	n.d.
841	0.09	ND	ND	ND	ND
2108	0.017	-----	-----	-----	0.080 PFHpA, 0.011 PfHxA
2115	0.070	-----	-----	-----	0.075 PFHpA
2129	0.02140	-----	-----	-----	-----
2131	0.01968185	-----	-----	-----	0.10895 PFHpA, 0.0144 PFHxA
2132	<0.1	<0.1	<0.1	<0.1	NA
2137	-----	-----	-----	-----	-----
2213	ND	ND	ND	ND	ND
2217	0.03792	-----	-----	n.a.	-----
2247	0.046	Not Detected	Not Detected	Not Detected	Not Detected
2255	n.d	n.d	n.d	n.d	n.d
2295	-----	-----	-----	-----	-----
2310	Not Detected	Not Detected	Not Detected	Not Detected	-----
2311	<0.1	-----	-----	-----	-----
2350	< 1.00	< 1.00	< 1.00	< 1.00	N/A
2352	-----	-----	-----	-----	-----
2357	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.
2363	<0.05	<0.05	<0.05	<0.05	<0.05
2365	<1.0	<1.0	<1.0	<1.0	<1.0
2366	<0.1	-----	-----	-----	-----
2370	< 1	< 1	< 1	< 1	< 1
2375	-----	-----	-----	-----	-----
2379	0.03	Not detected	Not detected	Not detected	-----
2380	<1.0	<1.0	<1.0	<1.0	<1.0
2382	<0.050	<0.050	<0.050	<0.050	<0.050
2386	0.02525	<0,001	<0,001	<0,001	0.00975
2390	-----	-----	-----	-----	-----
2462	-----	-----	-----	-----	-----
2508	-----	-----	-----	-----	0.1699 PFHpA
2560	ND	ND	ND	ND	ND
2561	0.029	-----	-----	-----	-----
2590	0.0230	-----	-----	-----	-----
2591	<0.05	-----	-----	-----	-----
2649	0.0255689	-----	-----	-----	-----
2675	0.023	< 0,003	< 0,001	< 0,002	0.091 PFHpA
2689	ND	-----	-----	-----	-----
2737	-----	-----	-----	-----	-----
2741	0.036	-----	-----	-----	-----
2743	0.2698	-----	-----	-----	0.6410 PFHpA
2798	-----	-----	-----	-----	-----
2804	<0.5	<0.5	<0.5	-----	<0.5
2812	-----	-----	-----	-----	-----
2886	0.0415	-----	-----	-----	-----
2912	-----	-----	-----	-----	-----
3100	<0.01	-----	-----	-----	-----
3116	-----	-----	-----	-----	-----
3118	-----	-----	-----	-----	-----
3146	20.0	-----	-----	-----	73.8 PFHpA
3149	-----	-----	-----	-----	0.2 PFHpA, 0.2 PFHxA
3153	<0.01	-----	-----	-----	-----
3154	0.02184	-----	-----	-----	0.01134 PFHxA
3172	<0.1	<0.1	<0.1	<0.1	-----
3176	-----	-----	-----	-----	-----
3185	<0.1	-----	-----	-----	-----
3197	ND	ND	ND	ND	-----
3200	-----	-----	-----	-----	-----
3210	0.0344	-----	-----	-----	-----
3214	<0.05	<0.05	<0.05	<0.05	-----
3218	-----	-----	-----	-----	-----
3220	ND	-----	-----	-----	-----
3237	-----	-----	-----	-----	-----
3248	0.52	-----	-----	-----	0.025

Determination of Total PFOA, Total PFNA, Total PFDA, Total PFBS and other Per-and Polyfluorinated substances on sample #20536; in mg/kg

lab	Total PFOA	Total PFNA	Total PFDA	Total PFBS	Other Per and Polyfluorinated substances
339	<0.1	-----	<0.1	-----	-----
840	n.d.	n.d.	n.d.	n.d.	n.d.
841	ND	ND	ND	ND	ND
2108	-----	-----	-----	-----	-----
2115	0.003	-----	-----	-----	0.065 PFHxS, 0.091 PFHpS
2129	0.006814	-----	-----	-----	-----
2131	0.0449295	-----	-----	-----	0.1208 PFHxS, 0.1277 PFHpS
2132	<0.1	<0.1	<0.1	<0.1	NA
2137	-----	-----	-----	-----	-----
2213	ND	ND	ND	ND	ND
2217	0.0079349	-----	-----	n.a.	-----
2247	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2255	n.d	n.d	n.d	n.d	n.d
2295	-----	-----	-----	-----	-----
2310	Not Detected	Not Detected	Not Detected	Not Detected	-----
2311	<0.1	-----	-----	-----	-----
2350	< 1.00	< 1.00	< 1.00	< 1.00	N/A
2352	-----	-----	-----	-----	-----
2357	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	n.d.	n.d.
2363	<0.05	<0.05	<0.05	<0.05	<0.05
2365	<1.0	<1.0	<1.0	<1.0	<1.0
2366	<0.1	-----	-----	-----	-----
2370	< 1	< 1	< 1	< 1	< 1
2375	-----	-----	-----	-----	-----
2379	0.03	Not detected	Not detected	Not detected	-----
2380	<1.0	<1.0	<1.0	<1.0	<1.0
2382	<0.050	<0.050	<0.050	<0.050	<0.050
2386	0.00484	<0,001	<0,001	0.00099	0.17097
2390	-----	-----	-----	-----	-----
2462	-----	-----	-----	-----	-----
2508	-----	-----	-----	-----	0.1143 PFHpS
2560	ND	ND	ND	ND	ND
2561	<0.025	-----	-----	-----	-----
2590	0.0210	-----	-----	-----	-----
2591	<0.05	-----	-----	-----	-----
2649	0.0141219	-----	-----	-----	-----
2675	0.004	< 0,003	< 0,001	< 0,002	0.169 PFHpS
2689	ND	-----	-----	-----	-----
2737	-----	-----	-----	-----	-----
2741	<0.02	-----	-----	-----	-----
2743	0.0868	-----	-----	-----	0.71 PFHxS, 22.9114 PFHpS
2798	-----	-----	-----	-----	-----
2804	<0.5	<0.5	<0.5	-----	<0.5
2812	-----	-----	-----	-----	-----
2886	-----	-----	-----	-----	-----
2912	-----	-----	-----	-----	-----
3100	<0.01	-----	-----	-----	-----
3116	-----	-----	-----	-----	-----
3118	-----	-----	-----	-----	-----
3146	5.2	-----	-----	-----	62 PFHxS, 80 PFHpS
3149	-----	-----	-----	-----	0.2 PFHxS, PFHpS
3153	<0.01	-----	-----	-----	-----
3154	0.00641	-----	-----	0.00086	0,05972 PFHxS, 0.00272 PFDS
3172	<0.1	<0.1	<0.1	<0.1	-----
3176	-----	-----	-----	-----	-----
3185	<0.1	-----	-----	-----	-----
3197	ND	ND	ND	ND	-----
3200	-----	-----	-----	-----	-----
3210	<0.01	-----	-----	-----	-----
3214	<0.05	<0.05	<0.05	<0.05	-----
3218	-----	-----	-----	-----	-----
3220	ND	-----	-----	-----	-----
3237	-----	-----	-----	-----	-----
3248	-----	-----	-----	-----	0.17

APPENDIX 3

Analytical details

lab	Accredited to ISO/IEC 17025	Sample intake	Technique to release/ extract the analyte(s)	Solvent used	Extraction Time	Extraction Temperature
339	No	---	---	---	---	---
840	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
841	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2108	Yes	0.5 g	Ultrasonic	Methanol	60 minutes	60°C
2115	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
2129	Yes	0.5 g	Ultrasonic	Methanol	30 minutes	room temp.
2131	Yes	2 g	Ultrasonic	Methanol	60 minutes	60°C
2132	No	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2137	No	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2213	Yes	1 g	Ultrasonic	Methanol	60 minutes	60°C
2217	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2247	Yes	2 g	Ultrasonic	Methanol	120 minutes	60°C
2255	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2295	Yes	2 g	Ultrasonic	Methanol	120 minutes	60°C
2310	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
2311	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2350	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2352	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2357	---	---	---	---	---	---
2358	Yes	0.5 g	Ultrasonic	Methanol	---	---
2363	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
2365	Yes	5mm*5mm	Ultrasonic	Methanol	120 minutes	60°C
2366	No	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2370	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2375	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2379	No	1 g	Ultrasonic	Methanol	120 minutes	60°C
2380	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
2382	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
2386	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
2390	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
2462	---	---	---	---	---	---
2508	Yes	0.5 g	Ultrasonic	Methanol	60 minutes	60°C
2560	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
2561	---	---	---	---	---	---
2590	---	---	---	---	---	---
2591	No	1 g	---	---	---	---
2649	Yes	---	Ultrasonic	Methanol	30 minutes	40°C
2675	No	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2689	No	0.5 g	Ultrasonic	Methanol	60 minutes	60°C
2737	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2741	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2743	Yes	1.5 g	Ultrasonic	Methanol	120 minutes	60°C
2798	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
2804	No	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2812	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
2886	No	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
2912	---	---	---	---	---	---
3100	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
3116	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
3118	---	---	---	---	---	---
3146	---	---	---	---	---	---
3149	Yes	2 g	Ultrasonic	Methanol	120 minutes	60°C
3153	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
3154	Yes	---	Ultrasonic	---	---	---
3172	---	---	---	---	---	---
3176	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
3185	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
3197	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
3200	No	0.5 g	Ultrasonic	Methanol	90 minutes	60°C
3210	Yes	2 g	Ultrasonic	Methanol	120 minutes	60°C
3214	Yes	0.5 g	Ultrasonic	Methanol	120 minutes	60°C
3218	Yes	1 g	Ultrasonic	Methanol	120 minutes	60°C
3220	Yes	1 g	Ultrasonic	Methanol	60 minutes	60°C
3237	Yes	1 g	Ultrasonic	Methanol	60 minutes	70°C
3248	---	---	---	---	---	---

APPENDIX 4

Number of participants per country

4 labs in	BANGLADESH
1 lab in	DENMARK
2 labs in	FRANCE
8 labs in	GERMANY
6 labs in	HONG KONG
1 lab in	HUNGARY
5 labs in	INDIA
1 lab in	INDONESIA
5 labs in	ITALY
14 labs in	P.R. of CHINA
1 lab in	PAKISTAN
2 labs in	SOUTH KOREA
1 lab in	SPAIN
1 lab in	SWITZERLAND
2 labs in	TAIWAN R.O.C.
1 lab in	THAILAND
6 labs in	TURKEY
1 lab in	UNITED KINGDOM
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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