Results of Proficiency Test Per-&Polyfluorinated Compounds in Textile March 2019

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. R.J. Starink
Correctors: ing. A.S. Noordman-de Neef & ing. C.M. Nijssen - Wester

Report: iis19A02

May 2019

CONTENTS

1 INTRODUCTION

Perfluorooctanoic acid (PFOA) is one important representative of the substance group of per- and polyfluorinated substances (PFASs). The hazard profile of PFOA is well known: PFOA is a persistent, bioaccumulative, and toxic (PBT-) 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) as Carc. 2, Repr. 1B and STOT RE 1 (liver). Due to its PBT and CMR properties, TOTAL PFOA and its ammonium salt (APFO) has been identified as substances of very high concern (SVHC) under REACH by unanimous agreement between EU Member States in 2014. Perfluorooctanesulfonic acid (PFOS) 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 Per-&Polyfluorinated Compounds in textile. During the annual proficiency testing program 2018/2019, it was decided to continue the proficiency test for the analysis of Per-&Polyfluorinated Compounds in textile. In this interlaboratory study 54 laboratories from 15 different countries registered for participation. See appendix 4 for the number of participants per country. In this report, the results of the 2019 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 analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. It was decided to send 2 different textile samples of 5 grams each and made of woven cotton, positive (artificially fortified) on PFOA, PFOS and/or PFDA (Perfluorodecanoic acid), labelled #19512 and #19513 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/IEC 17043:2010. 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

The first batch is a light brown colored cotton textile used for sample #19512 and was obtained from a third party laboratory. This batch was made positive on PFOS and was divided after cutting and homogenization over 60 plastic bags, approximately 5 grams each. The homogeneity of subsamples #19512 was checked by the determination of Total PFOS using an in-house method on eight stratified randomly selected samples. Please note that by the term "Total" is meant the sum of linear and branched isomers (see also paragraph 5).

	Total PFOS in mg/kg
sample #19512-1	4.80
sample #19512-2	4.95
sample #19512-3	4.85
sample #19512-4	4.82
sample #19512-5	4.73
sample #19512-6	4.73
sample #19512-7	4.34
sample #19512-8	4.76

Table 1: homogeneity test results of subsamples #19512

From the above test results, the repeatability was calculated and compared with 0.3 times the corresponding reproducibility of the reference method in agreement with the procedure of ISO 13528, Annex B2 in next table.

	Total PFOS in mg/kg
r (observed)	0.50
reference method	Horwitz (n=3)
0.3 * R (reference)	0.87

Table 2: evaluation of the repeatability of subsamples #19512

The second batch is a green colored cotton textile used for sample #19513 and was obtained from a third party laboratory. This batch was made positive on Total PFOA and Total PFDA and was divided after cutting and homogenization over 60 plastic bags, approximately 5 grams each. The homogeneity of subsamples #19513 was checked by the determination of Total PFOA and Total PFDA using an in-house method on eight stratified randomly selected samples. Please note that by the term “Total” is meant the sum of linear and branched isomers (see also paragraph 5).

	Total PFOA in mg/kg	Total PFDA in mg/kg
sample #19513-1	7.37	7.31
sample #19513-2	6.97	7.13
sample #19513-3	7.17	7.33
sample #19513-4	7.14	7.46
sample #19513-5	7.27	7.50
sample #19513-6	7.25	7.26
sample #19513-7	6.95	7.07
sample #19513-8	7.17	7.50

Table 3: homogeneity test results of subsamples #19513

From the above test results, the repeatabilities were calculated and compared with 0.3 times the corresponding reproducibility of the reference method in agreement with the procedure of ISO 13528, Annex B2 in next table.

	Total PFOA in mg/kg	Total PFDA in mg/kg
r (observed)	0.40	0.46
reference method	Horwitz (n=2)	Horwitz (n=2)
0.3 * R (reference)	1.01	1.03

Table 4: evaluation of the repeatabilities of subsamples #19513

The calculated repeatabilities for both samples are lower than 0.3 times the estimated reproducibility limits calculated using the Horwitz equation. Therefore, the homogeneity of the subsamples of #19512 and #19513 was assumed.

To each of the participating laboratories one sample #19512 and one sample #19513 was sent on February 13, 2019.

2.5 ANALYSES

The participants were asked to determine on samples #19512 and #19513: Perfluorooctanoic acid (Total PFOA), Perfluorooctanesulfonic acid (Total PFOS), Perfluorononanoic acid (Total PFNA), Perfluorodecanoic acid (Total PFDA) and ”other” per-&polyfluorinated substances, applying the analysis procedure that is routinely used in the laboratory. It was requested to report if the laboratory was accredited for the requested components that were determined. It was also requested to report some analytical details.

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 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 ISO 5725 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 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 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

In this interlaboratory study, no problems were encountered with the dispatch of the samples. Three participants reported test results after the final reporting date. Finally, the 54 reporting laboratories reported 189 numerical results. Observed were 5 outlying test results, which is 2.6%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

All original data sets given in appendix 1 proved to have a normal Gaussian distribution.

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this section, the results are discussed per sample and per component.
The test methods, which were used by various 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 listed in appendix 5.

For the determination of Per- and Polyfluorinated substances in textile, the CEN-TS 15968 method may be considered to be the official EC test method. Regretfully, the CEN-TS 15968 does not mention reproducibility requirements. Therefore, the target requirements in this study were estimated using the Horwitz equation based on two or three components (n=2 or n=3), see paragraph 5.

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

Sample #19512

Total PFOA: This determination was not problematic. No statistical outliers were observed. The calculated reproducibility is in agreement with the estimated reproducibility calculated using the Horwitz equation (2 components).

Total PFOS: This determination may be problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated reproducibility calculated using the Horwitz equation (3 components).

For other Per- and Polyfluorinated substances, 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 #19513

Total PFOA: This determination may be problematic. Two 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).

Total PFOS: This determination was not problematic. Two 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).

Total PFDA: This determination was not problematic. No statistical outliers were observed. The calculated reproducibility is in agreement with the estimated reproducibility calculated using the Horwitz equation (2 components).

For other Per- and Polyfluorinated substances, 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 test result, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility are presented in the next tables.

Component	unit	n	average	2.8 * sd	R(Horwitz)
Total PFOA	mg/kg	22	0.034	0.023	0.035
Total PFOS	mg/kg	52	4.80	3.39	2.94

Table 5: performance overview for sample #19512

Component	unit	n	average	2.8 * sd	R(Horwitz)
Total PFOA	mg/kg	51	5.86	3.59	2.84
Total PFOS	mg/kg	20	0.034	0.032	0.044
Total PFDA	mg/kg	39	5.43	2.90	2.67

Table 6: performance overview for sample #19513

Without further statistical calculations, it can be concluded that the group of participating laboratories have some problems with the analysis of Total PFOA and Total PFOS in textile. See also the discussion in paragraphs 4.1, 4.4 and 5.

4.3 COMPARISON OF PROFICIENCY TEST OF MARCH 2019 WITH PREVIOUS PTS.

	March 2019	March 2018	March 2017
Number of reporting labs	54	49	72
Number of results reported	189	132	263
Number of statistical outliers	5	8	17
Percentage outliers	2.6%	6.1%	6.5%

Table 7: comparison with previous proficiency tests

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

Table 8: development of relative 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 (2 or 3 components). The observed variation coefficient in this proficiency test on Total PFOA/Total PFOS in textile is larger compared to the observed variation coefficient of previous PTs. The observed RSD for Total PFDA (19%) is in line with the other 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.
It appeared that 74% of the participants mentioned to be accredited for the determination of Per-&Polyfluorinated substances in textile.
About 76% of the reporting participants mentioned to use test method CEN/TS 15968 for the determination of Total PFOA/Total PFOS/Total PFDA. About 20% of the participants reported to have used in house method and 4% of the reporting participants did not mention which test was used.
All participants used Ultrasonic technique to release/extract the analyte, except for two 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. It appeared that 39% of the participants reported to use 0.5 g and 44% of the participants reported to use 1 g. The effect of sample intake (0.5 g vs 1 g) was small and not significant: 4.79 vs 4.88 mg/kg respectively and variation RSD_R 24% vs 25% respectively, see also report iis18A02 of 2018.

5 DISCUSSION

In legislation and in the limits set to 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 this 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 were 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 Blue Sign regulations on Textiles (table 8), it is noticed that all of the reporting laboratories would reject sample #19512 and #19513 for containing too much Total PFOA, Total PFOS and/or Total PFDA.

	OEKO-TEX	Blue Sign BSSL v6.0
Total PFOA	<1.0 µg/m^2	<1.0 µg/m^2 (correspond with <0.01 mg/kg)
Total PFOS	<1.0 µg/m^2	<1.0 µg/m^2 (correspond 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

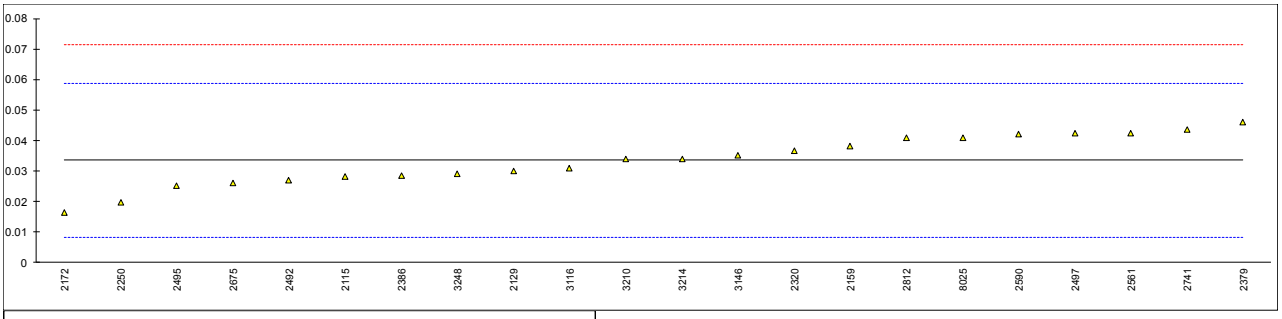
6 CONCLUSION

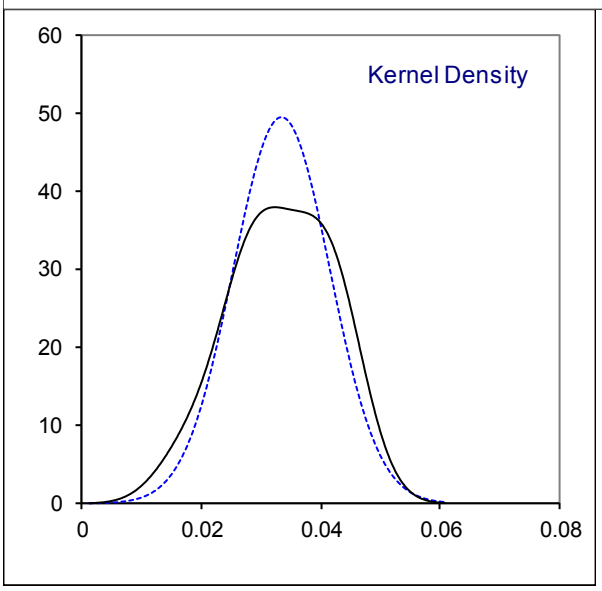
Each laboratory should evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

APPENDIX 1

Determination of Total PFOA on sample #19512; results in mg/kg

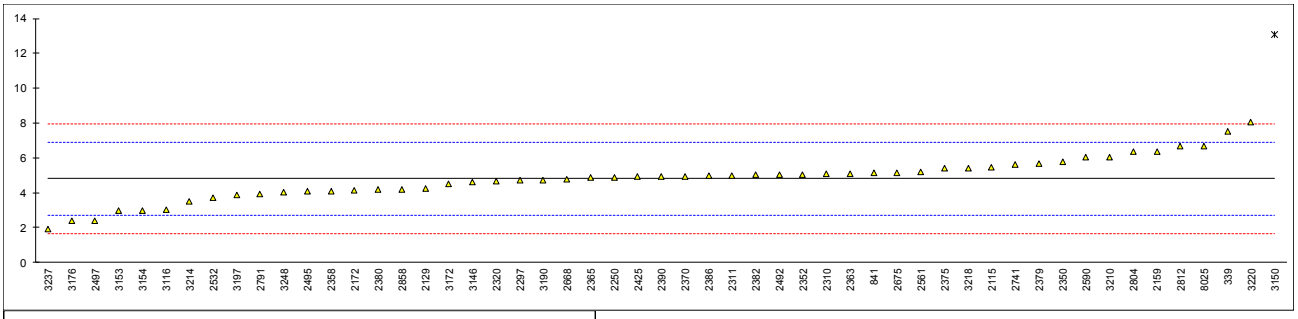
lab	method	value	mark	z(targ)	remarks
339	In house	<0.1		-----	
841	CEN-TS15968	ND		-----	
2115	CEN-TS15968	0.02823		-0.42	
2129	CEN-TS15968	0.0299		-0.28	
2159	In house	0.038		0.36	
2172	CEN-TS15968	0.0164		-1.35	
2250	CEN-TS15968	0.0198		-1.08	
2297	CEN-TS15968	<0.5		-----	
2310	CEN-TS15968	Not detected		-----	
2311	CEN-TS15968	Not detected		-----	
2320	CEN-TS15968	0.0367		0.25	
2350	CEN-TS15968	<1.00		-----	
2352		-----		-----	
2358	CEN-TS15968	n.d.		-----	
2363	CEN-TS15968	ND		-----	
2365	CEN-TS15968	<10		-----	
2370	CEN-TS15968	n.d.		-----	
2375	CEN-TS15968	<1		-----	
2379	CEN-TS15968	0.0459		0.98	
2380	CEN-TS15968	<0.025		-----	
2382		-----		-----	
2386	CEN-TS15968	0.0286		-0.39	
2390		-----		-----	
2425	In house	ND		-----	
2492	In house	0.027		-0.51	
2495	CEN-TS15968	0.025		-0.67	
2497	CEN-TS15968	0.042268	C	0.69	First reported 42.268 mg/kg
2532	CEN-TS15968	Not detected		-----	
2549		-----		-----	
2561	In house	0.0423		0.70	
2590	CEN-TS15968	0.042		0.67	
2668		ND		-----	
2675	CEN-TS15968	0.026		-0.59	
2741	CEN-TS15968	0.0436		0.80	
2791	CEN-TS15968	N.D		-----	
2804	In house	N.D.		-----	
2812	CEN-TS15968	0.041		0.59	
2858	In house	n.d		-----	
3116	CEN-TS15968	0.031		-0.20	
3146	CEN-TS15968	0.03526		0.14	
3150		-----		-----	
3153		-----		-----	
3154		-----		-----	
3172		-----		-----	
3176		-----		-----	
3190	CEN-TS15968	<0.1		-----	
3197	CEN-TS15968	ND		-----	
3210	CEN-TS15968	0.034		0.04	
3214	CEN-TS15968	0.034		0.04	
3218	CEN-TS15968	ND		-----	
3220	CEN-TS15968	ND		-----	
3237		-----		-----	
3248	In house	0.029		-0.36	
8025	In house	0.041		0.59	
	normality	OK			
	n	22			
	outliers	0			
	mean (n)	0.03350			
	st.dev. (n)	0.008080	RSD = 24%		
	R(calc.)	0.02262			
	st.dev.(Horwitz n=2)	0.012638			
	R(Horwitz n=2)	0.03539			

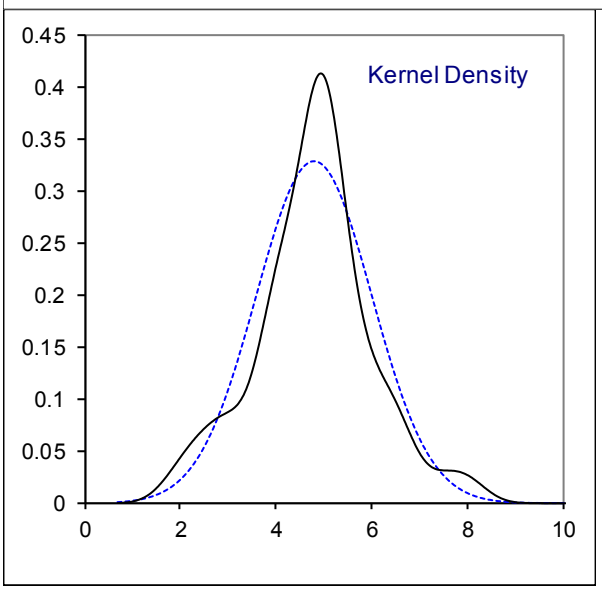

0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
2172
2250
2495
2675
2492
2115
2386
3248
2129
3116
3210
3214
3146
2320
2159
2812
8025
2590
2497
2561
2741
2379


Kernel Density
60
50
40
30
20
10
0
0
0.02
0.04
0.06
0.08

Determination of Total PFOS on sample #19512; results in mg/kg

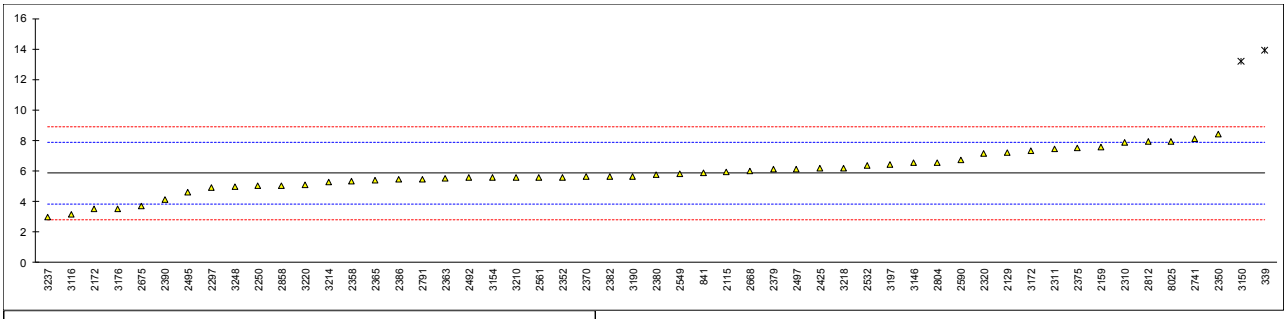
lab	method	value	mark	z(targ)	remarks
339	In house	7.509		2.57	
841	CEN-TS15968	5.12		0.30	
2115	CEN-TS15968	5.48		0.64	
2129	CEN-TS15968	4.224		-0.55	
2159	In house	6.37		1.49	
2172	CEN-TS15968	4.11		-0.66	
2250	CEN-TS15968	4.878		0.07	
2297	CEN-TS15968	4.73		-0.07	
2310	CEN-TS15968	5.09		0.27	
2311	CEN-TS15968	4.98		0.17	
2320	CEN-TS15968	4.6732		-0.12	
2350	CEN-TS15968	5.75		0.90	
2352	In house	5.04		0.23	
2358	CEN-TS15968	4.0849		-0.68	
2363	CEN-TS15968	5.1		0.28	
2365	CEN-TS15968	4.87		0.06	
2370	CEN-TS15968	4.93		0.12	
2375	CEN-TS15968	5.4		0.57	
2379	CEN-TS15968	5.6470		0.80	
2380	CEN-TS15968	4.2		-0.57	
2382	CEN-TS15968	5.01		0.20	
2386	CEN-TS15968	4.9693		0.16	
2390	CEN-TS15968	4.92		0.11	
2425	In house	4.91		0.10	
2492	In house	5.016		0.20	
2495	CEN-TS15968	4.057		-0.71	
2497	CEN-TS15968	2.40258	C	-2.28	First reported 2402.58 mg/kg
2532	CEN-TS15968	3.73		-1.02	
2549		-----		-----	
2561	In house	5.1729		0.35	
2590	CEN-TS15968	6.046		1.18	
2668	CEN-TS15968	4.77		-0.03	
2675	CEN-TS15968	5.149		0.33	
2741	CEN-TS15968	5.617		0.77	
2791	CEN-TS15968	3.94		-0.82	
2804	In house	6.35		1.47	
2812	CEN-TS15968	6.670		1.78	
2858	In house	4.20		-0.57	
3116	CEN-TS15968	3.00		-1.72	
3146	CEN-TS15968	4.623		-0.17	
3150	CEN-TS15968	13.08	R(0.01)	7.88	
3153	CEN-TS15968	2.96		-1.75	
3154		2.9674		-1.75	
3172	CEN-TS15968	4.5080		-0.28	
3176	In house	2.40		-2.29	
3190	CEN-TS15968	4.74		-0.06	
3197	CEN-TS15968	3.86		-0.90	
3210	CEN-TS15968	6.065		1.20	
3214	CEN-TS15968	3.486		-1.25	
3218	CEN-TS15968	5.407		0.57	
3220	CEN-TS15968	8.040	C	3.08	First reported 9.231
3237	CEN-TS15968	1.91		-2.75	
3248	In house	4.005		-0.76	
8025	In house	6.67		1.78	
	normality	OK			
	n	52			
	outliers	1			
	mean (n)	4.8030			
	st.dev. (n)	1.21133	RSD = 25%		
	R(calc.)	3.3917			
	st.dev.(Horwitz n=3)	1.05104			
	R(Horwitz n=3)	2.9429			

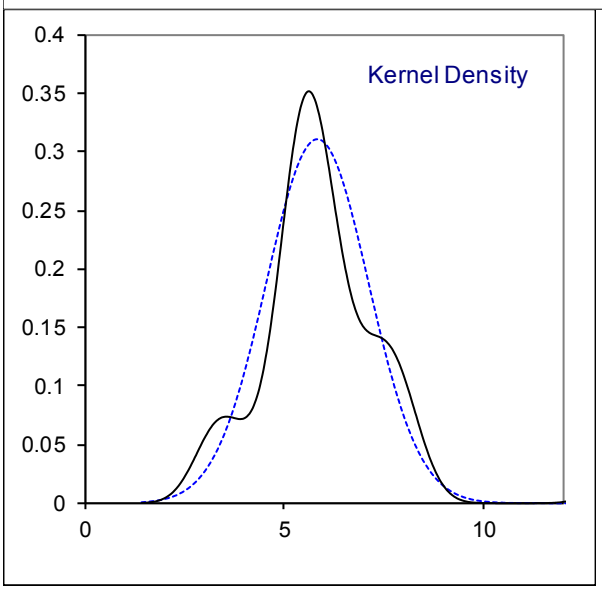

14
12
10
8
6
4
2
0
3237 3176 2497 3153 3154 3116 3214 2532 3197 2791 3248 2495 2358 2172 2380 2858 2129 3172 3146 2320 2297 3190 2668 2365 2250 2425 2390 2370 2386 2311 2382 2492 2352 2310 2363 841 2675 2561 2375 3218 2115 2741 2379 2350 2590 3210 2804 2159 2812 8025 339 3220 3150


Kernel Density
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0 2 4 6 8 10

Determination of Total PFOA on sample #19513; results in mg/kg

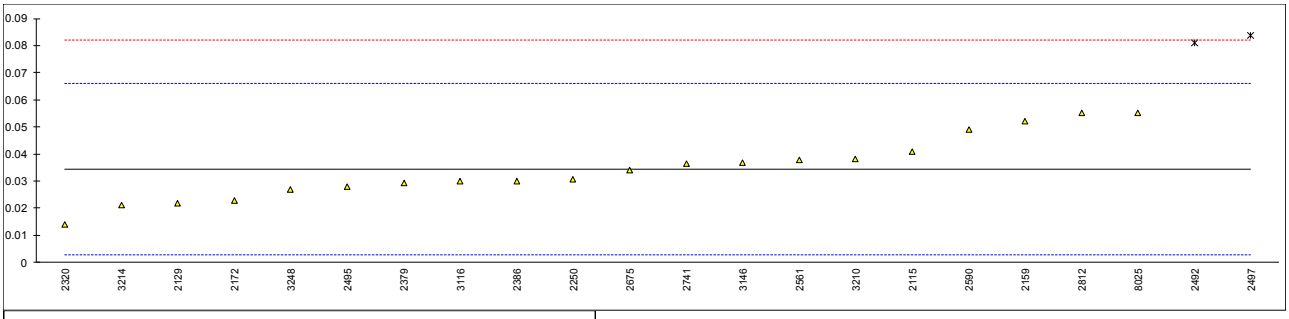
lab	method	value	mark	z(targ)	remarks
339	In house	13.89	R(0.01)	7.90	
841	CEN-TS15968	5.89		0.03	
2115	CEN-TS15968	5.94		0.08	
2129	CEN-TS15968	7.2212		1.34	
2159	In house	7.55		1.66	
2172	CEN-TS15968	3.51		-2.31	
2250	CEN-TS15968	5.004		-0.84	
2297	CEN-TS15968	4.93		-0.91	
2310	CEN-TS15968	7.90		2.01	
2311	CEN-TS15968	7.433		1.55	
2320	CEN-TS15968	7.1741		1.29	
2350	CEN-TS15968	8.44		2.54	
2352	In house	5.60		-0.26	
2358	CEN-TS15968	5.3204		-0.53	
2363	CEN-TS15968	5.5		-0.35	
2365	CEN-TS15968	5.42		-0.43	
2370	CEN-TS15968	5.61		-0.25	
2375	CEN-TS15968	7.5		1.61	
2379	CEN-TS15968	6.0907		0.23	
2380	CEN-TS15968	5.77		-0.09	
2382	CEN-TS15968	5.61		-0.25	
2386	CEN-TS15968	5.4376		-0.42	
2390	CEN-TS15968	4.10		-1.73	
2425	In house	6.2		0.34	
2492	In house	5.564		-0.29	
2495	CEN-TS15968	4.617		-1.22	
2497	CEN-TS15968	6.124781	C	0.26	First reported 6124.781 mg/kg
2532	CEN-TS15968	6.38		0.51	
2549	ISO23702-1	5.8		-0.06	
2561	In house	5.5962		-0.26	
2590	CEN-TS15968	6.736		0.86	
2668	CEN-TS15968	5.98		0.12	
2675	CEN-TS15968	3.687		-2.14	
2741	CEN-TS15968	8.082		2.19	
2791	CEN-TS15968	5.46		-0.39	
2804	In house	6.57	C	0.70	First reported N.D.
2812	CEN-TS15968	7.930		2.04	
2858	In house	5.04		-0.81	
3116	CEN-TS15968	3.16		-2.66	
3146	CEN-TS15968	6.5665		0.70	
3150	CEN-TS15968	13.20	R(0.01)	7.22	
3153		-----		-----	
3154		5.5721		-0.28	
3172	CEN-TS15968	7.3005		1.42	
3176	In house	3.52		-2.30	
3190	CEN-TS15968	5.61		-0.25	
3197	CEN-TS15968	6.41		0.54	
3210	CEN-TS15968	5.589		-0.27	
3214	CEN-TS15968	5.244		-0.61	
3218	CEN-TS15968	6.201		0.34	
3220	CEN-TS15968	5.080		-0.77	
3237	CEN-TS15968	2.96		-2.85	
3248	In house	4.965		-0.88	
8025	In house	7.93		2.04	
	normality	OK			
	n	51			
	outliers	2			
	mean (n)	5.8593			
	st.dev. (n)	1.28355	RSD = 22%		
	R(calc.)	3.5939			
	st.dev.(Horwitz n=2)	1.01604			
	R(Horwitz n=2)	2.8449			

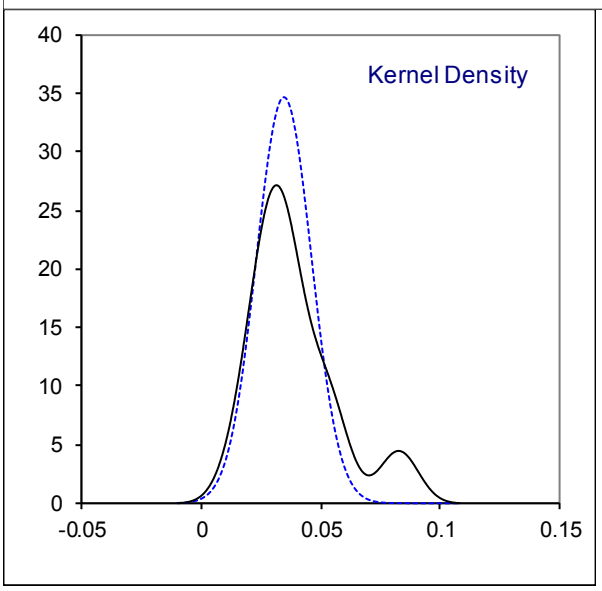

16
14
12
10
8
6
4
2
0
3237 3116 2172 3176 2675 2390 2495 2297 3248 2250 2858 3220 3214 2358 2365 2386 2791 2363 2492 3154 3210 2561 2352 2370 2382 3190 2380 2549 841 2115 2668 2379 2497 2425 3218 2532 3197 3146 2804 2590 2320 2129 3172 2311 2375 2159 2310 2812 8025 2741 2350 3150 339


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

Determination of Total PFOS on sample #19513; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	<0.1		-----	
841	CEN-TS15968	ND		-----	
2115	CEN-TS15968	0.0407		0.39	
2129	CEN-TS15968	0.0219		-0.79	
2159	In house	0.052		1.11	
2172	CEN-TS15968	0.023		-0.72	
2250	CEN-TS15968	0.0305		-0.25	
2297	CEN-TS15968	<0.5		-----	
2310	CEN-TS15968	Not Detected		-----	
2311	CEN-TS15968	Not Detected		-----	
2320	CEN-TS15968	0.0139		-1.30	
2350	CEN-TS15968	<1.00		-----	
2352		-----		-----	
2358	CEN-TS15968	n.d.		-----	
2363	CEN-TS15968	ND		-----	
2365	CEN-TS15968	<10		-----	
2370	CEN-TS15968	n.d.		-----	
2375	CEN-TS15968	<1		-----	
2379	CEN-TS15968	0.0292		-0.33	
2380	CEN-TS15968	<0.05		-----	
2382		-----		-----	
2386	CEN-TS15968	0.0301		-0.27	
2390		-----		-----	
2425	In house	ND		-----	
2492	In house	0.081	R(0.05)	2.94	
2495	CEN-TS15968	0.028		-0.41	
2497	CEN-TS15968	0.083831	C,R(0.05)	3.12	First reported 83.831 mg/kg
2532	CEN-TS15968	Not Detected		-----	
2549	ISO23702	ND		-----	
2561	In house	0.0377		0.20	
2590	CEN-TS15968	0.049		0.92	
2668		ND		-----	
2675	CEN-TS15968	0.034		-0.03	
2741	CEN-TS15968	0.0364		0.12	
2791	CEN-TS15968	N.D		-----	
2804	In house	N.D.	C	-----	First reported 6.57
2812	CEN-TS15968	0.055		1.30	
2858	In house	n.d		-----	
3116	CEN-TS15968	0.030		-0.28	
3146	CEN-TS15968	0.03663		0.14	
3150		-----		-----	
3153	CEN-TS15968	<0.1		-----	
3154		-----		-----	
3172		-----		-----	
3176		-----		-----	
3190	CEN-TS15968	<0.1		-----	
3197	CEN-TS15968	ND		-----	
3210	CEN-TS15968	0.038		0.22	
3214	CEN-TS15968	0.021		-0.85	
3218	CEN-TS15968	ND		-----	
3220	CEN-TS15968	ND		-----	
3237		-----		-----	
3248	In house	0.027		-0.47	
8025	In house	0.055		1.30	
	normality	OK			
	n	20			
	outliers	2			
	mean (n)	0.03445			
	st.dev. (n)	0.011485	RSD = 33%		
	R(calc.)	0.03216			
	st.dev.(Horwitz n=3)	0.015851			
	R(Horwitz n=3)	0.04438			

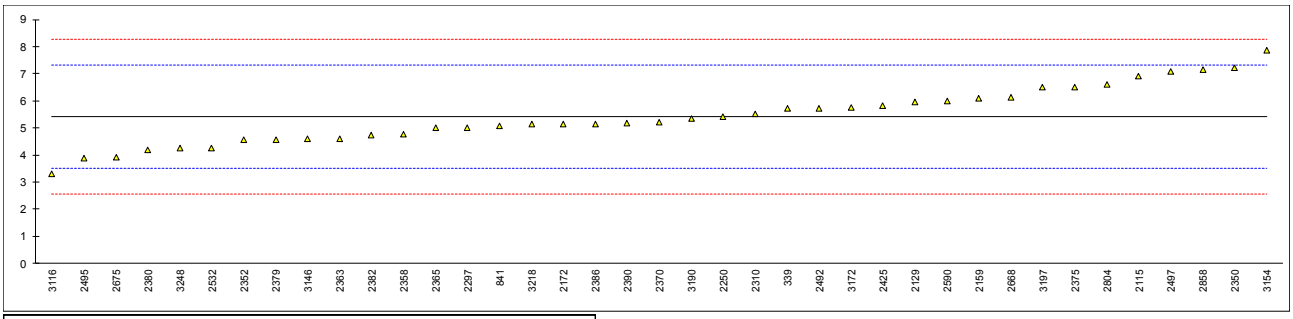

0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
2320
3214
2129
2172
3248
2495
2379
3116
2386
2250
2675
2741
3146
2561
3210
2115
2590
2159
2812
8025
2492
2497

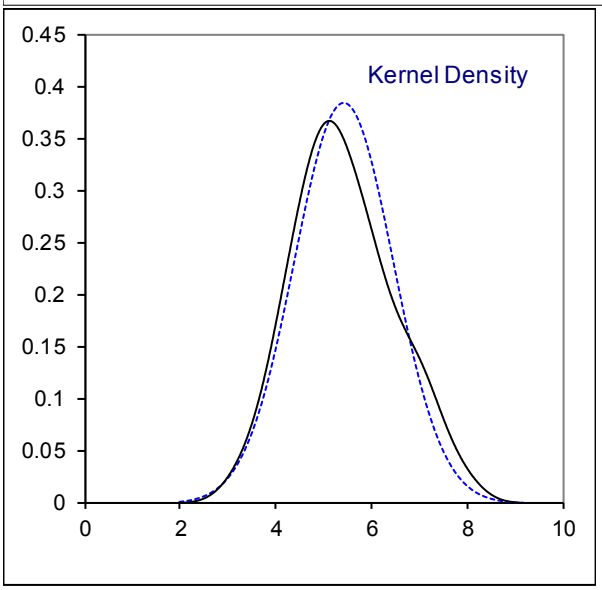

Kernel Density
40
35
30
25
20
15
10
5
0
-0.05
0
0.05
0.1
0.15

Determination of Total PFDA on sample #19513; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339		5.717		0.30	
841	CEN-TS15968	5.08		-0.37	
2115	CEN-TS15968	6.9060		1.55	
2129	CEN-TS15968	5.945		0.54	
2159	In house	6.09		0.70	
2172	CEN-TS15968	5.14		-0.30	
2250	CEN-TS15968	5.418		-0.01	
2297	CEN-TS15968	5.02		-0.43	
2310	CEN-TS15968	5.50		0.08	
2311		-----		-----	
2320		-----		-----	
2350	CEN-TS15968	7.22	C	1.88	First reported <1
2352	In house	4.55		-0.92	
2358	CEN-TS15968	4.7591		-0.70	
2363	CEN-TS15968	4.6		-0.87	
2365	CEN-TS15968	4.99		-0.46	
2370	CEN-TS15968	5.20		-0.24	
2375	CEN-TS15968	6.5		1.13	
2379	CEN-TS15968	4.5645		-0.91	
2380	CEN-TS15968	4.18		-1.31	
2382	CEN-TS15968	4.72		-0.74	
2386	CEN-TS15968	5.1525		-0.29	
2390	CEN-TS15968	5.16		-0.28	
2425	In house	5.82		0.41	
2492	In house	5.729		0.32	
2495	CEN-TS15968	3.879		-1.63	
2497	CEN-TS15968	7.080512	C	1.74	First reported 7080.512 mg/kg
2532	CEN-TS15968	4.26		-1.23	
2549		-----		-----	
2561		-----		-----	
2590	CEN-TS15968	6.006		0.61	
2668	CEN-TS15968	6.12		0.73	
2675	CEN-TS15968	3.905		-1.60	
2741		-----		-----	
2791		-----		-----	
2804	In house	6.59		1.22	
2812		-----		-----	
2858	In house	7.16		1.82	
3116	CEN-TS15968	3.32		-2.21	
3146	CEN-TS15968	4.5934		-0.88	
3150		-----		-----	
3153		-----		-----	
3154		7.8599		2.55	
3172	CEN-TS15968	5.7461		0.33	
3176		-----		-----	
3190	CEN-TS15968	5.33		-0.10	
3197	CEN-TS15968	6.49		1.12	
3210		-----		-----	
3214		-----		-----	
3218	CEN-TS15968	5.125		-0.32	
3220		-----		-----	
3237		-----		-----	
3248	In house	4.256		-1.23	
8025		-----		-----	

normality	OK
n	39
outliers	0
mean (n)	5.4277
st.dev. (n)	1.03605 RSD = 19%
R(calc.)	2.9009
st.dev.(Horwitz n=2)	0.95210
R(Horwitz n=2)	2.6659


9
8
7
6
5
4
3
2
1
0
3116
2495
2675
2380
3248
2532
2352
2379
3146
2363
2382
2358
2365
2297
841
3218
2172
2386
2390
2370
3190
2250
2310
339
2492
3172
2425
2129
2590
2159
2668
3197
2375
2804
2115
2497
2858
2350
3154


Kernel Density
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
2
4
6
8
10

APPENDIX 2: Other reported test results

Determination of Total PFNA, Total PFDA and other Per-and Polyfluorinated substances on sample #19512; in mg/kg

lab	Total PFNA	Total PFDA	Other
339	<0.1	<0.1	-----
841	ND	ND	-----
2115	-----	-----	-----
2129	<0,001	<0,001	PFHxS=0.0517 / PFHpS=0.0514 / PFDS=0.0114 / PFHxA=0.002 / PFHpA=0.0015
2159	-----	<0,01	PFHxS = 0.058 / PFHpS = 0.052
2172	-----	-----	-----
2250	<0.001	<0.001	PFHxS=0.0330 / PFHpS=0.0378 / PFDS=0.002 / PFHxA=0.002 / PFHpA=0.0115
2297	<0.5	<0.5	-----
2310	Not Detected	Not Detected	-----
2311	-----	-----	-----
2320	-----	-----	-----
2350	<1.00	<1.00	N/A
2352	-----	-----	-----
2358	n.d.	n.d.	n.d.
2363	ND	ND	ND
2365	<10	<10	-----
2370	n.d.	n.d.	n.d.
2375	-----	-----	-----
2379	Not detected	Not detected	-----
2380	<0.05	<0.05	-----
2382	-----	-----	-----
2386	0	0	0.1083
2390	-----	-----	-----
2425	ND	ND	-----
2492	-----	-----	-----
2495	<0.005	<0.005	PFHxS = 0.050 / PFHpS = 0.056
2497	-----	-----	0.99805
2532	Not Detected	Not Detected	Not Detected
2549	-----	-----	-----
2561	-----	-----	-----
2590	-----	-----	-----
2668	ND	ND	ND
2675	< 0,003	< 0,001	0.149
2741	-----	-----	-----
2791	-----	-----	-----
2804	N.D.	N.D.	N.D.
2812	-----	-----	-----
2858	n.d	n.d	-----
3116	-----	-----	-----
3146	-----	-----	-----
3150	-----	-----	-----
3153	-----	-----	-----
3154	-----	-----	-----
3172	-----	-----	-----
3176	-----	-----	-----
3190	<0.1	<0.1	-----
3197	ND	ND	-----
3210	-----	-----	-----
3214	-----	-----	-----
3218	ND	ND	ND
3220	-----	-----	-----
3237	-----	-----	-----
3248	-----	-----	0.085
8025	-----	-----	-----

Determination of Total PFNA and other Per-and Polyfluorinated substances on sample #19513; in mg/kg

lab	Total PFNA	Other
339	<0.1	-----
841	ND	-----
2115	-----	PFHpA=0.0478
2129	0.0041	PFHxA=0.014 / PFHpA=0.0818
2159	-----	PFHpA=0,083 / PF-3.6-DMOA=6,34
2172	-----	-----
2250	0.00230	PFHxA=0.00606 / PFHpA=0.0517
2297	<0.5	-----
2310	Not detected	-----
2311	-----	-----
2320	-----	-----
2350	<1.00	N/A
2352	-----	-----
2358	n.d.	n.d.
2363	ND	ND
2365	<10	-----
2370	n.d.	n.d.
2375	-----	-----
2379	Not detected	-----
2380	<0.05	-----
2382	-----	-----
2386	0.0028	0.0803
2390	-----	-----
2425	ND	-----
2492	-----	-----
2495	<0.005	PFHxS = 0.008 / PFHpS = 0.067
2497	-----	0.06864
2532	Not Detected	Not Detected
2549	-----	-----
2561	-----	-----
2590	-----	-----
2668	ND	ND
2675	0.007	0.141
2741	-----	-----
2791	-----	-----
2804	N.D.	N.D.
2812	-----	-----
2858	n.d	-----
3116	-----	-----
3146	-----	-----
3150	-----	-----
3153	-----	-----
3154	-----	-----
3172	-----	-----
3176	-----	-----
3190	<0.1	-----
3197	ND	-----
3210	-----	-----
3214	-----	-----
3218	ND	ND
3220	-----	-----
3237	-----	-----
3248	-----	0.081
8025	-----	-----

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	0.5	Ultrasonic	Methanol/ Toluene (50/50)	120	60
841	Yes	about 1g	Ultrasonic	Methanol	120	60
2115	Yes	0.5 grams	Ultrasonic	Methanol	120	60
2129	Yes	0,5 g	Ultrasonic	Methanol	30 min	Room temp
2159	No	1	Ultrasonic	Methanol	120	60
2172	Yes	1g	Ultrasonic	methanol	120	60
2250	Yes	4 g	Ultrasonic	Methanol	2 hours	60°C
2297	Yes	1g	Ultrasonic	methanol	120	60
2310	Yes	1g	Ultrasonic	Methanol	60	70
2311	Yes	0.5	Ultrasonic	Methanol	120	60
2320	Yes	1g	Ultrasonic	Methanol	120 min	60
2350	No	0.5g	Ultrasonic	Methanol	120	60
2352	Yes	1g	Ultrasonic	methanol	2h	60
2358	Yes	0.5 grams	Ultrasonic	Methanol	120 min	60 degree C
2363	Yes	1g	Ultrasonic	methanol	2 hours	60
2365	Yes	0.5g	Ultrasonic	Methyl alcohol	120min	60
2370	Yes	0.5 g	Ultrasonic	Methanol	120 min	60
2375	Yes	0.5 g	Ultrasonic	Methanol	120 min	60 °C
2379	No	1 g	Ultrasonic	MeOH	120 min	70 degree
2380	Yes	1.0 g	Ultrasonic	Methanol	120 minute	60 degree
2382	Yes	1.0g	Ultrasonic	Methanol	120min	60
2386	Yes	1 g	Ultrasonic	20 mL Methanol	120 min	60 °C
2390	Yes	1 g	Ultrasonic	Methanol	120 min ± 5	60 ±5
2425	Yes	1 gm	Ultrasonic	Methanol	2 h	60 ± 2°C
2492	Yes	0.5 gram	Ultrasonic	Methanol	60	60
2495	Yes	0.5 - 1 gram	Ultrasonic	Methanol	120	60
2497	Yes	2	Ultrasonic	methanol	60	60
2532	Yes	1 gram	Ultrasonic	Methanol	2 hours	60 °C
2549	---		---			
2561	Yes	0.5g	Ultrasonic	Methanol	60	40
2590	Yes	0.5 g	Ultrasonic	MeOH	2h	60°C
2668	Yes	0.5 g & 0.2g	Ultrasonic	Methanol	60 min	60°C
2675	No	0,5 g & 1 g	Ultrasonic	methanol	120 min	60°C
2741	No	0.5	Ultrasonic	Methanol	120	60
2791	Yes	0.5g	Ultrasonic	Methanol	120	60
2804	No	1	Ultrasonic	Methanol	120	60
2812	No	2	Ultrasonic	methanol	2 hours	60
2858	Yes	0.5	Ultrasonic	Methanol	60	60
3116	Yes	1 grams	Ultrasonic	methanol	120min	60°C
3146	Yes	1	Ultrasonic	Methanol	120	60
3150	No	1 and 0,5	Ultrasonic	Methanol	120	60
3153	Yes	0.5g	Ultrasonic	Methanol	120 min	60oC
3154	---		---			
3172	Yes	1.5	Ultrasonic	Methanol	120	60
3176	Yes	1 gram	Ultrasonic	Methanol	60 min	60
3190	No	2	Ultrasonic	methanol	120	60
3197	Yes	0,5 g	Ultrasonic	Methanol	120 minutes	60C
3210	No	0.500g	Ultrasonic	Methanol	90min	60°C
3214	Yes	2 grams	Ultrasonic	Methanol	120 mins	60°C
3218	Yes	3g	Ultrasonic	methanol	120min	60℃
3220	Yes	1 gm	Ultrasonic	Methanol	120 min	60 degree
3237	Yes	0,5 g	Ultrasonic	Methanol	120 min	60
3248	Yes	1	Ultrasonic	Methanol	120	60
8025	No	1	Ultrasonic	Methanol	120	60

APPENDIX 4

Number of participating laboratories per country:

3 labs in BANGLADESH
2 labs in FRANCE
7 labs in GERMANY
6 labs in HONG KONG
7 labs in INDIA
5 labs in ITALY
1 lab in KOREA
8 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in SRI LANKA
2 labs in TAIWAN R.O.C.
1 lab in THAILAND
7 labs in TURKEY
1 lab in UNITED KINGDOM
2 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

Literature

1. Analysis of the risks arising from the industrial use of Perfuorooctanoic acid (TOTAL PFOA) and Ammonium Perfluoro octanoate (APFO) and from their use in consumer articles. Evaluation of the risk reduction measures for potential restrictions on the manufacture, placing on the market and use of TOTAL PFOA and APFO, RPS (2010)
2. iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
3. ISO 13528:05
4. P.L. Davies, Fresenius Z. Anal. Chem, 331, 513-519 (1988)
5. ISO 5725:86
6. ISO 5725, parts 1-6:1994
7. M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
8. W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
9. Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), 165-172, (1983)
10. Analytical Methods Committee Technical Brief, No 4, January 2001
11. P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364 (2002)
12. NPR-CEN/TS 15968:10
13. ISO 25101:09
14. EM201:10
15. Directive 2006/122/EC of the European parliament and of the council of 12 December 2006 amending for the 30th time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulfonates).
16. S. Poothong, S.K. Boontanon and N. Boontanon, J. of Hazar. Mat., 205-206, 139-143 (2012)
17. PERFOOD report summary, EU project 227525 (2015), downloaded from http://cordis.europa.eu
18. Annex XV Restriction report, proposal for restriction, The German and Norwegian authorities, page 8, 17 October 2014, version 1.0
19. P. Supreeyasunthorn, S.K. Boontanon and N.Boontanon, J. Environ. Sci Health A. Tox Hazard Subst. Environ Eng, 51-6, 472-477 (2016)