Results of Proficiency Test
Total Per- & Polyfluorinated
Compounds in Polymers
August 2019

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Appendices:

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."

Since 2012, the Institute for Interlaboratory Studies organizes a proficiency scheme for the determination of Total Per- & Polyfluorinated Compounds in Polymers every year. During the annual proficiency testing program 2019/2020, it was decided to continue the proficiency test for the analysis of Total Per- & Polyfluorinated Compounds in Polymers.

In this interlaboratory study 31 laboratories in 16 different countries registered for participation. See appendix 4 for the number of participants per country. In this report, the test 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 (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory. It was decided to send two different samples of polymer labelled #19610 and #19611 of approximately 3 grams each. Both were artificially fortified on PFOS, PFOA and/or PFBS. The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation. Also, some analytical details were asked.

2.1   ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in accordance with ISO/IEC17043:2010 (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 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

Two different polymer batches both made of PVC were obtained from a third-party laboratory. Both batches were artificially fortified to be positive on some Per-/Polyfluorinated Compounds. Each batch was divided over 50 plastic bags of approximately 3 grams each. Each subsample of light yellow PVC squares was labelled #19610 and each subsample of pink PVC rings was labelled #19611.

The homogeneity of the subsamples #19610 was checked by determination of the PFOS and PFOA content according to an in-house test method on eight stratified randomly selected subsamples.

	PFOS in mg/kg	PFOA in mg/kg
sample #19610-1	161	1012
sample #19610-2	153	1008
sample #19610-3	164	1063
sample #19610-4	156	1041
sample #19610-5	157	1049
sample #19610-6	166	1059
sample #19610-7	155	1094
sample #19610-8	161	1072

Table 1: homogeneity test results of subsamples #19610

From the above test results the repeatability was calculated and compared with 0.3 times the target reproducibility, estimated from average PT uncertainties of previous PTs (see §4.1), in agreement with the procedure of ISO13528, Annex B2, in the next table.

	PFOS in mg/kg	PFOA in mg/kg
r (observed)	13	82
reference method	iis PTs, see §4.1	iis PTs, see §4.1
0.3 x R (reference method)	24	159

Table 2: evaluation of the repeatability of subsamples #19610

The calculated repeatability was in agreement with 0.3 times the target reproducibility. Therefore, homogeneity of the subsamples #19610 was assumed.

The homogeneity of the subsamples of #19611 was checked by determination of the PFOS and PFBS content according to an in-house test method on eight stratified randomly selected subsamples of #19611.

	PFOS in mg/kg	PFBS in mg/kg
sample #19611-1	414	512
sample #19611-2	424	538
sample #19611-3	403	524
sample #19611-4	395	487
sample #19611-5	403	516
sample #19611-6	396	520
sample #19611-7	386	492
sample #19611-8	415	483

Table 3: homogeneity test results of subsamples #19611

From the above test results the repeatability was calculated and compared with 0.3 times the target reproducibility, estimated from average PT uncertainties of previous PTs (see §4.1), in agreement with the procedure of ISO13528, Annex B2, in the next table.

	PFOS in mg/kg	PFBS in mg/kg
r (observed)	35	55
reference method	iis PTs, see §4.1	iis PTs, see §4.1
0.3 x R (reference method)	61	77

Table 4: evaluation of the repeatability of subsamples #19611

The calculated repeatability was in agreement with 0.3 times the target reproducibility. Therefore, homogeneity of the subsamples #19611 was assumed.

To each of the participating laboratories a set of 1 subsample #19610 and 1 subsample #19611 was sent on August 7, 2019.

2.5   ANALYZES

The participants were requested to determine on both samples #19610 and #19611 the total of: PFOA, PFOS, PFNA, PFDA, PFBS and to report 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' test 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 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 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 reanalyzis). Additional or corrected test results are used for data analyzis and the original reported test results are placed under 'Remarks' in the test result tables in appendix 1 or 2. 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 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 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 data set 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 them 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. 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 variation in this interlaboratory study.

The target standard deviation was calculated from the target reproducibility by division with 2.8. In case no literature reproducibility was available, other target values are 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. 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 proficiency test, no problems were encountered with the dispatch of the samples. Four participants did not report any test results at all. Finally, the 27 reporting laboratories reported 130 numerical results. Observed were 7 outlying test results, which is 5.4%. 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 test results are discussed per sample and per component. The test methods, which were used by the various laboratories were taken into account for explaining the observed differences when possible and applicable. These test methods are also in the tables in appendix 1 together with the original data. The abbreviations used in these tables are listed in appendix 5.

For the determination of PFOA/PFOS in textile method CEN/TS15968 is considered to be the official EC test method by the majority of the participating laboratories. However, test method CEN/TS15968 does not mention reproducibility requirements.
Therefore, since the 2018 PT, 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 to 2018, see table 6.

Also, no official test method exists for the determination of PFNA, PFDA or PFBS. It was decided to use the same target reproducibility of 18% for these components.

In test method CEN/TS15968 chapter 8 it is stated that for polymers and granulates it is recommended to use ISO6427. In ISO6427 table 1 and 2 several extraction methods dependent on the type of polymers is listed. It is recommended to use Soxhlet for extraction of PVC samples. Therefore, the test results from participants that did not use Soxhlet for extraction were excluded from the statistical evaluations, see also §5 and appendix 1.

Sample #19610

PFOA: This determination was problematic. Two statistical outliers were observed and eleven other test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility found in previous iis PTs.

PFOS: This determination was problematic. Three statistical outliers were observed and thirteen other test results were excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility found in previous iis PTs.

For PFNA, PFDA, PFBS and other Per- & Polyfluorinated substances the majority of the participants agreed on a concentration near or below the limit of detection, see appendix 2. The material had not been spiked with these components. Therefore, it was decided not to calculate z-scores for these determinations.

Sample #19611

PFOS: This determination was not problematic. One statistical outlier was observed and thirteen other test results were excluded. However, the calculated reproducibility after rejection of the suspect data is in full agreement with the estimated reproducibility found in previous iis PTs.

PFBS: This determination was problematic. One statistical outlier was observed and eight other test results were excluded. 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, see appendix 2. 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 FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility estimated from previous iis PTs and the reproducibility as found for the group of participating laboratories. The number of significant test results, the average result, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility derived from previous iis PTs are presented in the next table.

Component	unit	n	average	2.8 * sd	R(target)
PFOA in #19610	mg/kg	12	910	516	459
PFOS in #19610	mg/kg	11	121	73	61
PFOS in #19611	mg/kg	13	356	182	179
PFBS in #19611	mg/kg	10	405	297	204

Table 5: reproducibilities of tests on samples #19610 and #19611

Without further statistical calculations, it can be concluded that there is no good compliance of the group of participating laboratories with the target reproducibilities. The problematic tests have been discussed in §4.1.

4.3 COMPARISON OF PROFICIENCY TEST OF AUGUST 2019 WITH PREVIOUS PTS

The observed variation expressed as the relative standard deviation RSD of the test results in the 2019 PT is in line with the observations in previous PTs, see below table.

Component	2019	2018	2017	2016	2015 -2012	iis Target
PFOS	18-21%	22%	13-24%	19%	24%	18%
PFOA	20%	21%	20%	18%	29-30%	18%
PFNA	n.d.	34%	n.d.	n.d.	n.d.	18%
PFBS	26%	n.d.	n.d.	n.d.	n.d.	18%

Table 6: development of uncertainties over the years

The uncertainties for PFOS and PFOA is in line with previous iis PTs. The uncertainty of PFBS is in line with the one of PFNA, both new components in an iis PT.

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 reporting participants (n=27) the following can be summarized:
- a majority of 19 participants (≈70%) reported to be accredited for this test in accordance with ISO/IEC17025 for determination of Per- & Polyfluorinated Compounds in polymers.
- 20 participants mentioned that they have further cut/grinded the samples before use and 5 participants mentioned to have used the samples as received.
- regarding the extraction technique that was used about two equally sized groups of participants can be distinguished: one group that used Soxhlet (n=14) and one other group (n=11) that used Ultrasonic for extraction.

- all participants mentioned to have used Methanol in combination with or without Dichloromethane or Toluene as extraction solvent.
- the participants that used Soxhlet extraction used an extraction time of 6-8 hours, while the extraction time used by the Ultrasonic participants was 1-2 hours.
- the median extraction temperature was 60°C within a range of 40-120°C.

The effect of extraction technique on the determination is further discussed in §5.

5   DISCUSSION

The CEN/TS15968 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. For grinding of polymers and granulates CEN/TS15968 method refers to ISO6427 and to ISO9113. However, after sample pre-treatment about half of the participants continue following CEN/TS15968 method with Ultrasonic extraction technique while the other half of the participants continue to follow ISO6427 with Soxhlet extraction.

Participants that did not use Soxhlet extraction were excluded from the statistical evaluation to get a good estimation of the consensus value of the components which were added to the polymers. The Soxhlet extraction technique yields higher levels of Per- & Polyfluorinated Compounds in polymers with less variation in the test results, see table 7 for an example for the PFOS component in both PT samples. Please note that this effect could also come from the extraction time that is inherent to the extraction technique being used; Soxhlet 6-8 hours vs. Ultrasonic 1-2 hours, see also §4.4.

Analytical Details	Sample	unit	n	average	2.8 * sd	RSD (%)
Ultrasonic extraction	#19610	mg/kg	9	110	123	40
Soxhlet extraction	#19610	mg/kg	11	121	73	21
Ultrasonic extraction	#19611	mg/kg	9	140	412	105
Soxhlet extraction	#19611	mg/kg	13	356	182	18

Table 7: reproducibility of PFOS in polymers

6   CONCLUSION

The conclusion is that many of the participants has some difficulty with the determination of Total Per- & Polyfluorinated Compounds. The total levels of Per- & Polyfluorinated Compounds that can be extracted from polymers is highly dependent on the chosen 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 PFOA on sample #19610; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	1960.94	DG(0.01)	6.42	
339	In house	807.995	ex	-0.62	
826	CEN-TS15968	987.1	ex	0.47	
840	In house	896.3		-0.08	
841	CEN-TS15968	559.081	ex	-2.14	
2138	CEN-TS15968	998.4	ex	0.54	
2241	In house	918.8	ex	0.05	
2295		-----		-----	
2320	CEN-TS15968	786.44		-0.75	
2350	In house	891.8		-0.11	
2352	In house	728.82		-1.11	
2358	CEN-TS15968	848.338		-0.38	
2363	CEN-TS15968	734		-1.07	
2365	EPA3540C/8321B	756.795		-0.94	
2379	CEN-TS15968	1099.18		1.16	
2382	CEN-TS15968	756.000		-0.94	
2384	CEN-TS15968	1195.13		1.74	
2386	CEN-TS15968	800.14	ex	-0.67	
2390	CEN-TS15968	965.72		0.34	
2492	In house	491.36	ex	-2.56	
2590	CEN-TS15968	1261.2630		2.14	
2737	CEN-TS15968	2175.0	C,DG(0.01)	7.72	first reported 3105.7
2773	CEN-TS15968	439.12	ex	-2.87	
2841		-----		-----	
2886		-----		-----	
3150		-----		-----	
3154	In house	320.03	ex	-3.60	
3163		-----		-----	
3172	CEN-TS15968	319.6	ex	-3.60	
3210		-----		-----	
3248	In house	403.3	ex	-3.09	

				all participants:	
normality	OK			OK	
n	12			23	
outliers	2 +11ex			2	
mean (n)	909.982			781.074	
st.dev. (n)	184.4295	RSD=20%		261.2626	RSD=33%
R(calc.)	516.403			731.535	
st.dev.(iis)	163.7968			140.5934	
R(iis)	458.631			393.662	
Compare					
R(Horwitz)	206.751	(2 components)		181.590	

ex= test result excluded when no Soxhlet extraction was used, see paragraph 4.1 and 5
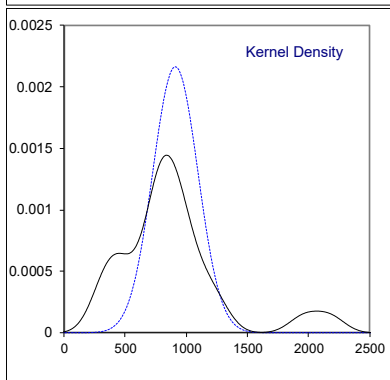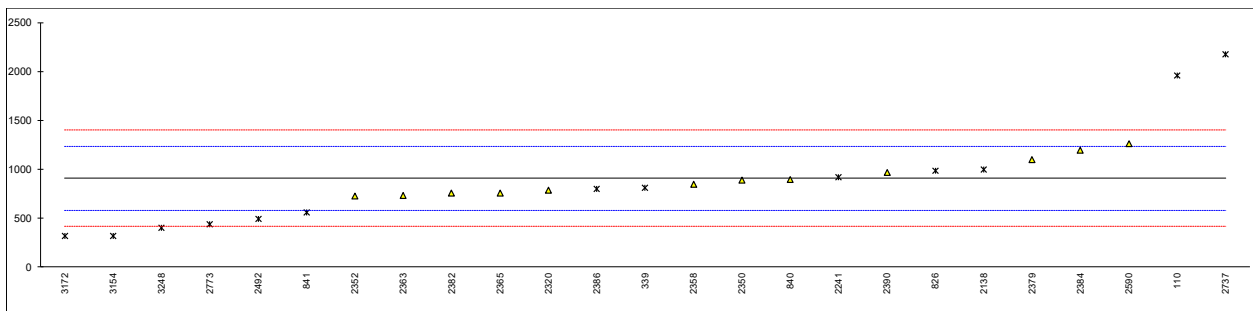
Determination of PFOS on sample #19610; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	365.88	G(0.01)	11.24	
339	In house	150.347	ex	1.35	
826	CEN-TS15968	168.0	ex	2.16	
840	In house	127.6		0.30	
841	CEN-TS15968	78.574	ex	-1.95	
2138	CEN-TS15968	146.5	ex	1.17	
2241	In house	60.7	ex	-2.77	
2295		-----		-----	
2320	CEN-TS15968	126.65		0.26	
2350	In house	134.6		0.62	
2352	In house	115.94		-0.23	
2358	CEN-TS15968	109.814		-0.51	
2363	CEN-TS15968	120		-0.05	
2365	EPA3540C/8321B	104.095		-0.78	
2379	CEN-TS15968	81.38	C	-1.82	first reported 237.12
2382	CEN-TS15968	110.000		-0.51	
2384	CEN-TS15968	186.49		3.01	
2386	CEN-TS15968	120.7615	ex	-0.01	
2390	CEN-TS15968	114.61		-0.29	
2492	In house	63.07	ex	-2.66	
2590	CEN-TS15968	249.88	C,DG(0.05)	5.92	first reported 364.151
2737	CEN-TS15968	213.02	DG(0.05)	4.22	
2773	CEN-TS15968	2301	ex,C	100.08	first reported 1918.16
2841		-----		-----	
2886	In house	137.47	ex	0.76	
3150	CEN-TS15968	12188	ex	553.97	
3154	In house	44.43	ex,C	-3.52	first reported 28.70
3163		-----		-----	
3172	CEN-TS15968	53.9	ex	-3.08	
3210		-----		-----	
3248	In house	89.3	ex	-1.46	

				all participants:	
	normality	not OK		OK	
	n	11		24	
	outliers	3 +13ex		3	
	mean (n)	121.016		121.130	
	st.dev. (n)	25.9200	RSD=21%	49.3214	RSD=41%
	R(calc.)	72.576		138.100	
	st.dev.(iis)	21.7829		21.8035	
	R(iis)	60.992		61.050	
Compare					
	R(Horwitz)	45.623	(3 components)	45.660	

ex= test result excluded when no Soxhlet extraction was used, see paragraph 4.1 and 5
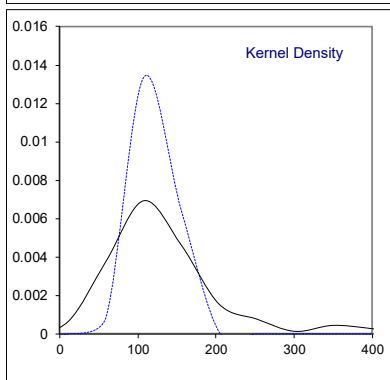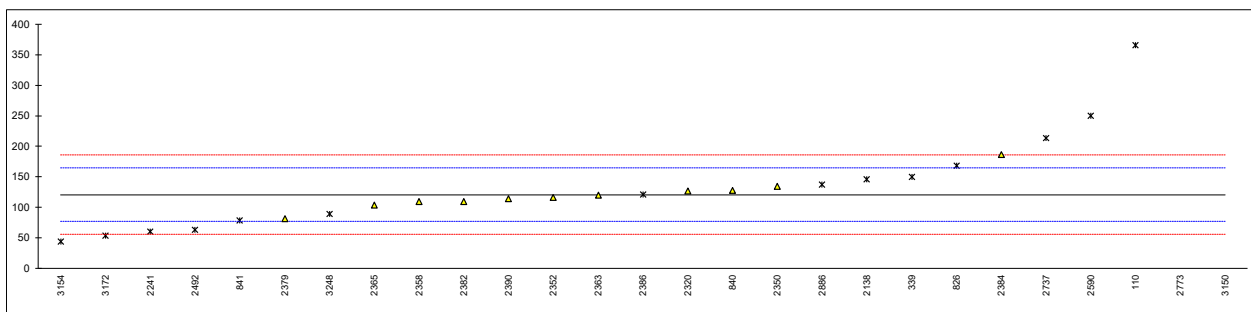
Determination of PFOS on sample #19611; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	1079.04	G(0.01)	11.29	
339	In house	297.786	ex,C	-0.91	first reported 0.275
826	CEN-TS15968	295.3	ex	-0.95	
840	In house	377.2		0.33	
841	CEN-TS15968	255.795	ex	-1.56	
2138	CEN-TS15968	254.7	ex	-1.58	
2241	In house	327.4	ex	-0.44	
2295		-----		-----	
2320	CEN-TS15968	399.66		0.68	
2350	In house	340.3		-0.24	
2352	In house	324.08		-0.50	
2358	CEN-TS15968	353.797		-0.03	
2363	CEN-TS15968	345		-0.17	
2365	EPA3540C/8321B	328.043		-0.43	
2379	CEN-TS15968	242.64	C	-1.77	first reported 685.9
2382	CEN-TS15968	324.000		-0.50	
2384	CEN-TS15968	518.43	C	2.54	first reported 603.55
2386	CEN-TS15968	18.371	ex	-5.27	
2390	CEN-TS15968	307.60		-0.75	
2492	In house	12.66	ex	-5.36	
2590	CEN-TS15968	351.5560		-0.07	
2737	CEN-TS15968	414.1		0.91	
2773	CEN-TS15968	808	ex,C	7.06	first reported 674.62
2841		-----		-----	
2886	In house	24	ex,C	-5.18	first reported 19
3150	CEN-TS15968	2215	ex	29.02	
3154	In house	8.73	ex,C	-5.42	first reported 4.43
3163		-----		-----	
3172	CEN-TS15968	9.04	ex	-5.41	
3210		-----		-----	
3248	In house	21.3	ex	-5.22	

				all participants:	
normality	not OK			OK	
n	13			24	
outliers	1 +13ex			3	
mean (n)	355.877			256.312	
st.dev. (n)	64.8872	RSD=18%		152.5601	RSD=60%
R(calc.)	181.684			427.168	
st.dev.(iis)	64.0579			46.1362	
R(iis)	179.362			129.181	
Compare					
R(Horwitz)	114.059	(3 components)			

ex= test result excluded when no Soxhlet extraction was used, see paragraph 4.1 and 5
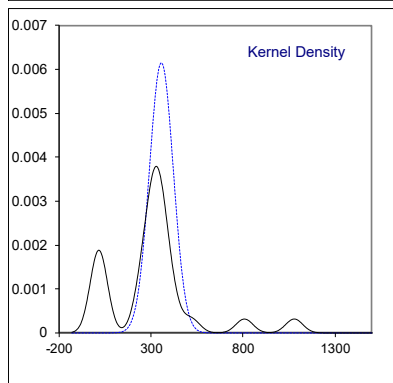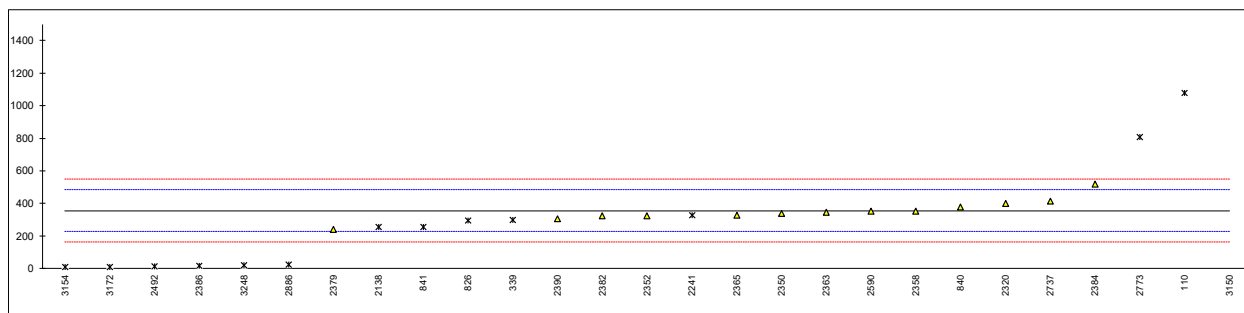
Determination of PFBS on sample #19611; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	985.23	D(0.01)	7.97	
339		-----		-----	
826		-----		-----	
840	In house	504.8		1.37	
841	CEN-TS15968	367.326	ex	-0.51	
2138	CEN-TS15968	NA		-----	
2241	In house	375.2	ex	-0.41	
2295		-----		-----	
2320		out of cap		-----	
2350	In house	425.4		0.28	
2352	In house	384.52		-0.28	
2358	CEN-TS15968	543.153		1.90	
2363	CEN-TS15968	378		-0.37	
2365	EPA3540C/8321B	393.175		-0.16	
2379	CEN-TS15968	195.33	C	-2.87	first reported N.D.
2382	CEN-TS15968	383.000		-0.30	
2384		-----		-----	
2386	CEN-TS15968	30.893	ex	-5.13	
2390	CEN-TS15968	532.78		1.76	
2492	In house	27.32	ex	-5.18	
2590	CEN-TS15968	307.8410		-1.33	
2737		-----		-----	
2773	CEN-TS15968	49.2	ex,C	-4.88	first reported 41.46
2841		-----		-----	
2886		-----		-----	
3150		-----		-----	
3154	In house	21.06	ex	-5.27	
3163		-----		-----	
3172	CEN-TS15968	23.02	ex	-5.24	
3210		-----		-----	
3248	In house	49.9	ex	-4.87	

				all participants:
normality	OK			OK
n	10			18
outliers	1 +8ex			1
mean (n)	404.800			277.329
st.dev. (n)	105.9158	RSD=26%		193.7978	RSD=70%
R(calc.)	296.564			542.634
st.dev.(iis)	72.8640			49.9192
R(iis)	204.019			139.774
Compare				
R(Horwitz)	103.897	(2 components)		

ex= test result excluded when no Soxhlet extraction was used, see paragraph 4.1 and 5
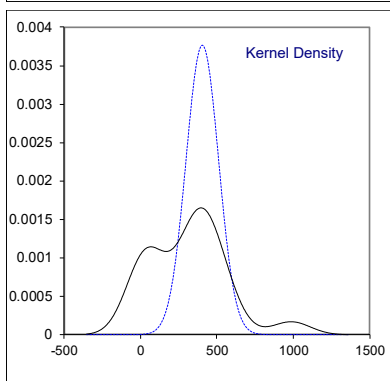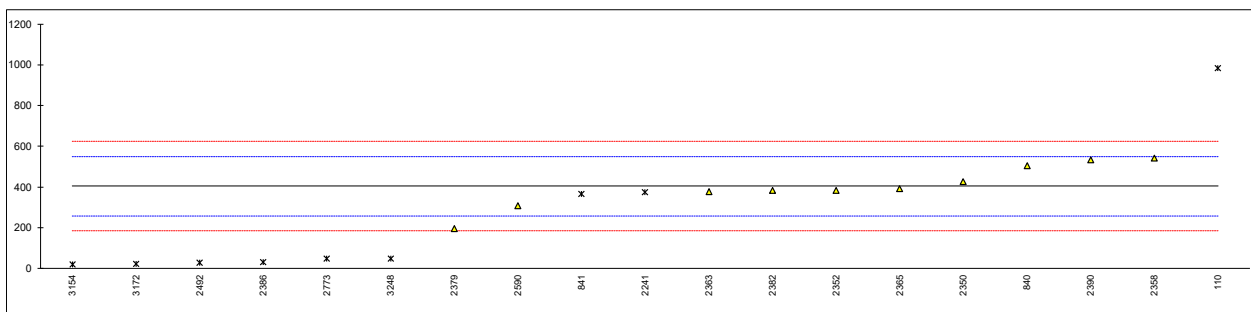
APPENDIX 2 Other reported test results

Determination of PFNA, PFDA and PFBS on sample #19610; results in mg/kg

lab	method	PFNA	mark	PFDA	mark	PFBS	mark
110	In house	0.199		ND		ND	
339		-----		-----		-----	
826		-----		-----		-----	
840	In house	n.d.		n.d.		n.d.	
841	CEN-TS15968	<0.025		<0.025		<0.025	
2138	CEN-TS15968	NA		NA		NA	
2241	In house	<0.1		<0.1		83.4	C, f+?
2295		-----		-----		-----	
2320	CEN-TS15968	out of cap		out of cap		out of cap	
2350	In house	<1.00		<1.00		<1.00	
2352		-----		-----		-----	
2358	CEN-TS15968	n.d.		n.d.		n.d.	
2363	CEN-TS15968	ND		ND		ND	
2365	EPA3540C/8321B	＜0.025		＜0.025		＜0.025	
2379	CEN-TS15968	ND		ND		ND	
2382	CEN-TS15968	<0.05		<0.05		<0.05	
2384	CEN-TS15968	<10		-----		-----	
2386		-----		-----		-----	
2390	CEN-TS15968	ND		ND		ND	
2492	In house	0.03		-----		-----	
2590	CEN-TS15968	0.0610		-----		0.0280	
2737		-----		-----		-----	
2773	CEN-TS15968	0.024		ND		ND	
2841		-----		-----		-----	
2886		-----		-----		-----	
3150		-----		-----		-----	
3154	In house	-----		-----		0.01	
3163		-----		-----		-----	
3172	CEN-TS15968	< 0.1		< 0.1		< 0.1	
3210		-----		-----		-----	
3248	In house	0.032		-----		0.007	

Lab 2241 first reported 52.2

Lab 2241 possibly a false positive test result?

Determination of Other Per- and Polyfluorinated substances on sample #19610; results in mg/kg

lab	method	value
110	EPA3540C/8321B	87.62
339		-----
826		-----
840		-----
841	CEN-TS15968	<0.025
2138	CEN-TS15968	NA
2241		-----
2295		-----
2320	CEN-TS15968	out of cap
2350	In house	N/A
2352		-----
2358	CEN-TS15968	N/A
2363		-----
2365		-----
2379		-----
2382	CEN-TS15968	<0.05
2384		-----
2386		-----
2390	CEN-TS15968	ND
2492	In house	34.46
2590		-----
2737		-----
2773	CEN-TS15968	PFHxA-1.84mg/kg; PFHpA-15.4mg/kg; PFHxS-17.4mg/kg
2841		-----
2886		-----
3150		-----
3154	In house	0,86 PFHxA; 7,11 PFHpA; 4,89 PFHxS
3163		-----
3172	CEN-TS15968	PFHpa: 6.15mg/Kg; PFHpS: 3.239mg/Kg; PFHxA: 0.626mg/Kg; PFHxS: 9.91mg/Kg
3210		-----
3248	In house	33.9

Determination of PFOA, PFNA and PFDA on sample #19611; results in mg/kg

lab	method	PFOA	mark	PFNA	mark	PFDA	mark
110	In house	1.1110		ND		ND	
339	In house	0.275	C	-----		-----	
826		-----		-----		-----	
840	In house	n.d.		n.d.		n.d.	
841	CEN-TS15968	0.405		<0.025		<0.025	
2138	CEN-TS15968	ND		NA		NA	
2241	In house	<0.1		<0.1		<0.1	
2295		-----		-----		-----	
2320	CEN-TS15968	N.D		out of cap		out of cap	
2350	In house	<1.00		<1.00		<1.00	
2352	In house	0.33		-----		-----	
2358	CEN-TS15968	n.d.		n.d.		n.d.	
2363	CEN-TS15968	0.35		ND		ND	
2365	EPA3540C/8321B	0.316		＜0.025		＜0.025	
2379	CEN-TS15968	ND		ND		ND	
2382	CEN-TS15968	0.351		<0.05		<0.05	
2384	CEN-TS15968	<10		<10		-----	
2386	CEN-TS15968	0.2845		-----		-----	
2390	CEN-TS15968	1.12		ND		ND	
2492	In house	0.165		-----		-----	
2590	CEN-TS15968	1.5720		1.0710		0.0570	
2737		-----		-----		-----	
2773	CEN-TS15968	ND		ND		ND	
2841		-----		-----		-----	
2886		-----		-----		-----	
3150	CEN-TS15968	126362	f+?	-----		-----	
3154	In house	0.08		-----		-----	
3163		-----		-----		-----	
3172	CEN-TS15968	< 0.1		< 0.1		< 0.1	
3210		-----		-----		-----	
3248	In house	0.242		-----		-----	

Lab 339 first reported 297.786

Lab 3150 possibly a false positive test result?

Determination of Other Per- and Polyfluorinated substances on sample #19611; results in mg/kg

lab	method	value	mark
110	EPA3540C/8321B	169.13	possibly a false positive test result?
339		-----	
826		-----	
840		-----	
841	CEN-TS15968	<0.025	
2138	CEN-TS15968	NA	
2241		-----	
2295		-----	
2320		-----	
2350	In house	N/A	
2352		-----	
2358	CEN-TS15968	N/A	
2363		-----	
2365		-----	
2379		-----	
2382	CEN-TS15968	<0.05	
2384		-----	
2386		-----	
2390		-----	
2492	In house	2.8	
2590		-----	
2737		-----	
2773	CEN-TS15968	PFHxS=7.30	
2841		-----	
2886		-----	
3150		-----	
3154	In house	1.91 PFHxS	
3163		-----	
3172	CEN-TS15968	PFHxS: 1.953 mg/Kg	
3210		-----	
3248	In house	7.0	

APPENDIX 3   Analytical details

lab	Accredited acc. to ISO /IEC17025	Sample pre-treatment prior to analyzis	Type of extraction	Solvent(s) for extraction	Time extraction (min)	Temperature extraction (°C)
110	Yes	Further Cut	Soxhlet	Methanol:DCM 1:1	360	55
339	No	Further Cut	Ultrasonic	Methanol/Toluene	120	60
826	No	Further Grinded	Ultrasonic	Methanol	120	60
840	Yes	Further Cut	Soxhlet	Methanol:DCM 1:1	120	---
841	---	---	---	---	---	---
2138	Yes	Used as received	Ultrasonic	Methanol	120	40
2241	Yes	Further Cut	Ultrasonic	Methanol:DCM 1:1	120	60
2295	---	---	---	---	---	---
2320	Yes	Further Cut	Soxhlet	Methanol:DCM 1:1	360	---
2350	No	Further Cut	Soxhlet	Methanol:DCM 1:1	360	70
2352	Yes	Further Cut	Soxhlet	Methanol:DCM 1:1	360	---
2358	Yes	Further Cut	Soxhlet	Methanol:DCM 1:1	360	80
2363	Yes	Further Cut	Soxhlet	Methanol:DCM 1:1	360	---
2365	Yes	Further Cut	Soxhlet	Methanol/DCM	60	120
2379	No	Further Cut	Soxhlet	Methanol:DCM 1:1	360	100
2382	Yes	Further Cut	Soxhlet	Methanol:DCM 1:1	480	---
2384	Yes	Further Grinded	Soxhlet	Methanol:DCM 1:1	360	Reflux temp.
2386	Yes	Used as received	Ultrasonic	Methanol	120	60
2390	Yes	Further Cut	Soxhlet	Methanol/DCM	360	45-50
2492	Yes	Further Cut	Ultrasonic	Methanol	60	60
2590	Yes	Further Grinded	Soxhlet	Methanol:DCM 1:1	360	---
2737	Yes	Used as received	Soxhlet	Methanol/DCM	360	105
2773	Yes	Further Cut	Ultrasonic	Methanol	120	60
2841	---	---	---	---	---	---
2886	No	Used as received	Ultrasonic	Methanol	120	Minimum 60
3150	No	Further Cut	Ultrasonic	Methanol	120	60
3154	---	---	---	---	---	---
3163	---	---	---	---	---	---
3172	Yes	Further Cut	Ultrasonic	Methanol	120	60
3210	---	---	---	---	---	---
3248	Yes	Used as received	Ultrasonic	Methanol	120	60

APPENDIX 4

Number of participants per country

1 lab in   DENMARK
2 labs in   FRANCE
4 labs in   GERMANY
3 labs in   HONG KONG
1 lab in   INDIA
2 labs in   ITALY
1 lab in   MALAYSIA
6 labs in   P.R. of CHINA
1 lab in   PAKISTAN
3 labs in   SOUTH KOREA
1 lab in   SRI LANKA
1 lab in   THAILAND
1 lab in   THE NETHERLANDS
1 lab in   TURKEY
1 lab in   U.S.A.
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

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