Results of Proficiency Test
Total Per- & Polyfluoroalkyl
Substances (PFAS) in Polymers
September 2021

Organized 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 Polyfluoroalkyl Substances (PFAS). 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 PFAS 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. Perfluorooctanesulfonic acid (PFOS) is listed as persistent organic pollutant (POP) in Annex B of the Stockholm Convention. To protect health and environment, the European Union published Directive 2006/122/EC on 27 December 2006 to restrict the placing on the market and the use of Per- and Polyfluoroalkyl Substances. In the following years these products came under more scrutiny and subsequently the limits for the presence of these products were further restricted. In July 2020 regulation EU 2020/784 was implemented for PFOA and its related compounds. The limits published for substances, articles and mixtures is 0.025 mg/kg for PFOA and 1 mg/kg for individual related PFOA compounds or a combination of those compounds. Higher limits are allowed if the current limits cannot be met, however the aim should be to lower the amount of PFAS. For PFOS the limit is published in regulation EU 2019/1021 and is 10 mg/kg for substances or mixtures and 0.1%M/M for semi-finished products and articles or parts thereof.

Since 2012 the Institute for Interlaboratory Studies organizes a proficiency scheme for the determination of Total Per- and Polyfluoroalkyl Substances (PFAS) in polymers every year. Total means the sum of linear and branched isomers per type of PFAS. During the annual proficiency testing program 2021/2022, it was decided to continue the proficiency test for the analysis of Total PFAS in Polymers.

In this interlaboratory study 39 laboratories in 19 different countries registered for participation. See appendix 4 for the number of participants per country. In this report the test 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 (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 positive on some Per- and Polyfluoroalkyl Substances labelled #21710 and #21711 of approximately 3 grams each.
The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement 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

For the first sample a batch of grey PVC blocks fortified with PFOS was selected. After homogenization 80 subsamples in small bags of 3 gram each were filled and labelled #21710.
The homogeneity of the subsamples was checked by determination of the Total PFOS content according to method CEN/TS15968 on eight stratified randomly selected subsamples.

	Total PFOS in mg/kg
sample #21710-1	691
sample #21710-2	660
sample #21710-3	672
sample #21710-4	651
sample #21710-5	688
sample #21710-6	674
sample #21710-7	682
sample #21710-8	668

Table 1: homogeneity test results of subsamples #21710

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 paragraph 4.1) in agreement with the procedure of ISO13528, Annex B2, in the next table.

	Total PFOS in mg/kg
r (observed)	38
reference method	iis PTs
0.3 x R (reference method)	102

Table 2: evaluation of the repeatability of subsamples #21710

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

For the second sample a batch of yellow PVC rings fortified with PFOA and PFBS. (Polyfluorobutanesulfonic acid), was selected. After homogenization 80 subsamples in small bags of 3 gram each were filled and labelled #21711.
The homogeneity of the subsamples was checked by determination of the Total PFOA and Total PFBS content according to an in-house test method on eight stratified randomly selected subsamples.

	Total PFOA in mg/kg	Total PFBS in mg/kg
sample #21711-1	458	454
sample #21711-2	470	436
sample #21711-3	465	456
sample #21711-4	453	472
sample #21711-5	447	453
sample #21711-6	450	465
sample #21711-7	463	467
sample #21711-8	478	470

Table 3: homogeneity test results of subsamples #21711

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

	Total PFOA in mg/kg	Total PFBS in mg/kg
r (observed)	30	33
reference method	iis PTs	iis PTs
0.3 x R (reference method)	70	69

Table 4: evaluation of the repeatabilities of subsamples #21711

The calculated repeatabilities were in agreement with 0.3 times the corresponding target reproducibility. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one subsample #21710 and one subsample #21711 was sent on August 18, 2021.

2.5 ANALYZES

The participants were requested to determine on both samples the total of each individual PFAS: Perfluorooctanoic acid (PFOA), Perfluorooctanesulfonic acid (PFOS), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), Perfluorobutanesulfonic acid (PFBS), Perfluorooctadecanoic acid (PFODA), Perfluorododecanoic acid (PFDoA) and to report other Per- and Polyfluorinated substances. Also, some analytical details were requested to be reported. Total means the sum of linear and branched isomers per type of PFAS.

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 reference test methods (when applicable) 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 reanalysis). Additional or corrected test results are used for data analysis and the original test results are placed under 'Remarks' in the 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.

The assigned value is determined by consensus based on the test results of the group of participants after rejection of the statistical outliers and/or suspect data.

According to ISO13528 all (original received or corrected) results per determination were submitted to outlier tests. In the iis procedure for proficiency tests, outliers are detected prior to calculation of the mean, standard deviation and reproducibility. For small data sets, Dixon (up to 20 test results) or Grubbs (up to 40 test results) outlier tests can be used. For larger data sets (above 20 test results) Rosner's outlier test can be used. 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. 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 (dotted line) was projected over the Kernel Density Graph (smooth line) for reference. The Gauss curve is calculated from the consensus value and the corresponding standard deviation.

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 (e.g. ISO or ASTM test methods), 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 literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values are used, like Horwitz or an estimated reproducibility based on former iis proficiency tests.

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:

$$z_{(target)} = (\text{test result - average of PT}) / \text{target standard deviation}$$

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:

$$|z| < 1 \quad \text{good}$$
$$1 < |z| < 2 \quad \text{satisfactory}$$
$$2 < |z| < 3 \quad \text{questionable}$$
$$3 < |z| \quad \text{unsatisfactory}$$

4   EVALUATION

In this interlaboratory study some problems were encountered with the dispatch of the samples due to the COVID-19 pandemic. Therefore, the reporting time on the data entry portal was extended with one week. Four participants reported test results after the extended reporting date. Three participants did not report any test results and not all participants were able to report all components requested.
Finally, 36 reporting laboratories submitted 98 numerical test results. Observed were 2 outlying test results, which is 2.0%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Not all 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 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 together with the original data in appendix 1. The abbreviations used in these tables are explained in appendix 5.

For the determination of PFOS in coated and impregnated solid articles, liquids and firefighting foams, 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.
Since the 2018 PT it was decided to use a relative target standard deviation of 18% for this PT based on iis PT data of PFOA/PFOS proficiency tests from 2016 to 2018 (see the report iis18P08 on www.iisnl.com on the News and Reports page). In the PTs of 2018, 2019 and 2020 this RSD is confirmed, so an iis PT target RSD of 18% is still applicable.
Also, no official test method exists for the determination of the other PFAS. It was decided to use the same target standard deviation 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 are 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 for more discussion also paragraph 5 and appendix 1.

Sample #21710
Total PFOS: This determination was not problematic. One statistical outlier was observed and nineteen other test results were excluded. The calculated reproducibility after rejection of the suspect data is in full agreement with the estimated reproducibility found in previous iis proficiency tests.

The majority of the participants agreed on a concentration near or below the limit of detection for the other PFAS. Therefore, it was decided not to calculate z-scores for these determinations. The reported test results are given in appendix 2.

Sample #21711
Total PFOA: This determination was not problematic. One statistical outlier was observed and nineteen other test results were excluded. The calculated reproducibility after rejection of the suspect data is in good agreement with the estimated reproducibility found in previous iis proficiency tests.

Total PFBS: This determination was not problematic. No statistical outliers were observed and seventeen other test results were excluded. The calculated reproducibility after rejection of the suspect data is in agreement with the estimated reproducibility found in previous iis proficiency tests.

The majority of the participants agreed on a concentration near or below the limit of detection for the other PFAS. Therefore, it was decided not to calculate z-scores for these determinations. The reported test results 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 reference test method 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 target reproducibility based on previous iis proficiency tests are presented in the next table.

Component	unit	n	average	2.8 * sd	R(target)
Total PFOS	mg/kg	15	701	382	353

Table 5: reproducibility of test on samples #21710

Component	unit	n	average	2.8 * sd	R(target)
Total PFOA	mg/kg	15	306	134	154
Total PFBS	mg/kg	11	416	135	209

Table 6: reproducibilities of tests on samples #21711

Without further statistical calculations, it can be concluded that there is a good compliance of the group of participating laboratories with the target reproducibilities.

4.3   COMPARISON OF PROFICIENCY TEST OF SEPTEMBER 2021 WITH PREVIOUS PTS

	September 2021	September 2020	August 2019	September 2018	September 2017
Number of reporting laboratories	36	36	27	32	35
Number of test results	98	88	130	118	119
Number of statistical outliers	2	5	7	1	10
Percentage of statistical outliers	2.0%	5.7%	5.4%	0.8%	8.4%

Table 7: comparison with previous proficiency tests

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

The performance of the determinations of the proficiency tests was compared, expressed as relative standard deviation (RSD) of the PTs, see next table.

Component	2021	2020	2019	2018	2017 -2012	iis Target
Total PFOS	19%	27%	18-21%	22%	19-24%	18%
Total PFOA	16%	22%	20%	21%	18-30%	18%
Total PFNA	n.d.	n.d.	n.d.	34%	n.d.	18%
Total PFBS	12%	n.d.	26%	n.d.	n.d.	18%
Total PFDoA	n.d.	31%	n.d.	n.d.	n.d.	18%

Table 8: development of relative uncertainties over the years

The uncertainties observed in this PT for PFOA, PFOS and PFBS are the same as or smaller than previous PTs.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this proficiency test some analytical details were requested. The answers are given in appendix 3. Based on the answers given by the reporting participants the following can be summarized:
- 26 participants (≈75%) reported to be accredited in accordance with ISO/IEC17025 for the determination of Per- & Polyfluoroalkyl Substances in polymers.
- 25 participants mentioned that they have further cut/grinded the samples before use and 9 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=16) and one other group (n=17) that used Ultrasonic for extraction. One laboratory used a Stirrer.
- 32 participants mentioned to have used Methanol in combination with or without Dichloromethane as extraction solvent. One participant mentioned to have used Methanol and water.
- the participants that used Soxhlet extraction used an extraction time of 6-8 hours at a temperature of 60-70°C or 1-2 hours at a temperature higher than 100°C, while the extraction time used by the Ultrasonic participants was 1-2 hours at a temperature of 60°C.

The effect of extraction technique on the determination is further discussed in paragraph 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, which has been discussed in previous reports. 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 paragraph 4.4.

In this report "total" means the sum of linear and branched isomers per type of PFAS. In previous proficiency tests iis has observed that some laboratories could report linear and branched PFAS components. For simplicity iis decided to evaluate only the total of each PFAS component present in the samples. See for more detail PT report iis17P08 on PFAS in polymers. This report can be downloaded for free from the iis general website www.iisnl.com.

6   CONCLUSION

The conclusion is that many of the participants has some difficulty with the total determination of individual Per- & Polyfluoroalkyl Substances. The total levels of PFAS 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.
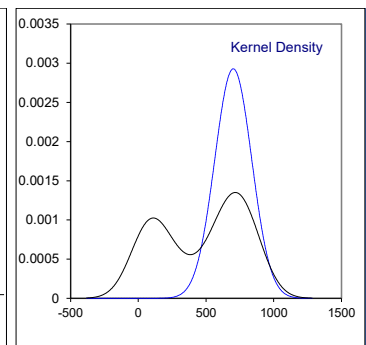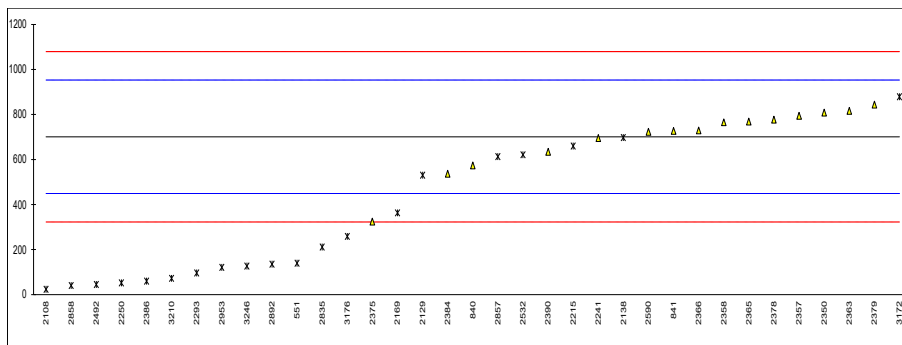
APPENDIX 1

Determination of PFOS (Polyfluorooctanesulfonic acid) on sample #21710; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	<100		<-4.76	Possibly a false negative test result?
551	In house	139.435	G(0.05)	-4.45	
840		573.4		-1.01	
841	CEN-TS15968	727		0.21	
2108	In house	23.38	ex	-5.37	
2129	In house	530	ex	-1.35	
2138	KS M9722	697	ex	-0.03	
2169	CEN-TS15968	362.49	ex	-2.68	
2215	In house	659.17	ex	-0.33	
2241	CEN-TS15968	695.01		-0.05	
2250	CEN-TS15968	51.6	ex	-5.15	
2293	CEN-TS15968	95.60	ex	-4.80	
2295		-----		-----	
2350	In house	807.91		0.85	
2357	EN15968	794.0		0.74	
2358	CEN-TS15968	765.4		0.51	
2363	EPA3540C/8321B	816.1		0.91	
2365	In house	768.12		0.53	
2366	CEN-TS15968	728.9		0.22	
2375	In house	324		-2.99	
2378	CEN-TS15968	777		0.60	
2379	CEN-TS15968	843.524		1.13	
2384	CEN-TS15968	536.4776		-1.30	
2386	CEN-TS15968	59.47	ex	-5.08	
2390	CEN-TS15968	633.57		-0.53	
2492	In house	44.33	ex	-5.20	
2532	CEN-TS15968	620.6	ex	-0.64	
2590	CEN-TS15968	723.167		0.18	
2749		-----		-----	
2835	In house	211	ex	-3.88	
2857	CEN-TS15968	612.53	ex	-0.70	
2858	In house	40.00	ex	-5.24	
2892	CEN-TS15968	135.000	ex	-4.49	
2953	CEN-TS15968	120.459	ex	-4.60	
3172	CEN-TS15968	878.25	ex	1.41	
3176	CEN-TS15968	258.2	ex	-3.51	
3210	In house	71.84	ex	-4.99	
3246	CEN-TS15968	126	ex	-4.56	
3248		-----		-----	

				All participants:	
	normality	not OK		OK	
	n	15		35	
	outliers	1 (+19ex)		0	
	mean (n)	700.905		464.284	
	st.dev. (n)	136.2967	RSD = 19%	304.5075	RSD = 66%
	R(calc.)	381.631		852.621	
	st.dev.(iis)	126.1629		83.5711	
	R(iis)	353.256		233.999	
comp					
	R(Horwitz)	202.854	(3 components)	142.966	

Ex = test result excluded when Soxhlet extraction was not used, see paragraph 4.1 and 5

Determination of PFOA (Polyfluorooctanoic acid) on sample #21711; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	350	ex	0.79	
551	In house	92.849	G(0.05)	-3.87	
840		284.9		-0.39	
841	CEN-TS15968	284		-0.41	
2108	In house	91.46	ex	-3.90	
2129	In house	400	ex	1.70	
2138	KS M9722	369	ex	1.14	
2169	CEN-TS15968	316.89	ex	0.19	
2215	In house	237.21	ex	-1.25	
2241	CEN-TS15968	385.35		1.43	
2250	CEN-TS15968	103.8	ex	-3.67	
2293	CEN-TS15968	195.0	ex	-2.02	
2295		-----		-----	
2350	In house	380.38		1.34	
2357	EN15968	289.0		-0.31	
2358	CEN-TS15968	277.2		-0.53	
2363	EPA3540C/8321B	285.6		-0.38	
2365	In house	280.57		-0.47	
2366	CEN-TS15968	295		-0.21	
2375	In house	328		0.39	
2378	CEN-TS15968	289		-0.31	
2379	CEN-TS15968	320.397		0.25	
2384	CEN-TS15968	211.0524		-1.73	
2386	CEN-TS15968	131.93	ex	-3.16	
2390	CEN-TS15968	388.69		1.49	
2492	In house	93.61	ex	-3.86	
2532	CEN-TS15968	575.01	ex	4.87	
2590	CEN-TS15968	296.174		-0.18	
2749		-----		-----	
2835		-----		-----	
2857	CEN-TS15968	346.80	ex	0.73	
2858	In house	105.00	ex	-3.65	
2892	CEN-TS15968	200.000	ex	-1.93	
2953	CEN-TS15968	146.647	ex	-2.90	
3172	CEN-TS15968	1031.32	ex	13.15	
3176	CEN-TS15968	332.2	ex	0.47	
3210	In house	158.89	ex	-2.67	
3246	CEN-TS15968	195	ex	-2.02	
3248		-----		-----	

All participants:

normality	OK			OK
n	15			34
outliers	1 (+19ex)			1
mean (n)	306.354			265.783
st.dev. (n)	47.8001	RSD = 16%		110.4228 RSD = 42%
R(calc.)	133.840			309.184
st.dev.(iis)	55.1438			47.8409
R(iis)	154.403			133.954
comp				
R(Horwitz)	81.998	(2 components)		72.676

Ex = test result excluded when Soxhlet extraction was not used, see paragraph 4.1 and 5
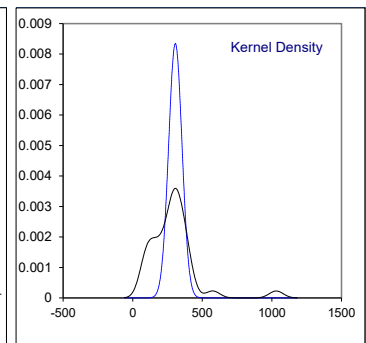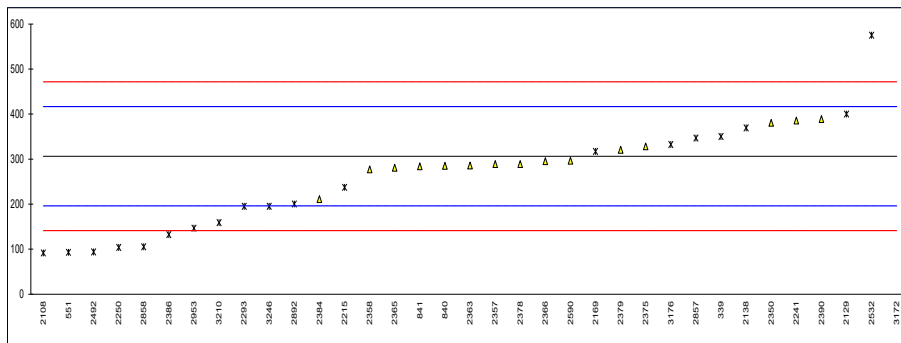
Determination of PFBS (Perfluorobutanesulfonic acid) on sample #21711; results in mg/kg

lab	method	value	mark	z(targ)	remarks
339	In house	355	ex	-0.81	
551		-----		-----	
840		454.0		0.51	
841	CEN-TS15968	466		0.67	
2108	In house	136.71	ex	-3.73	
2129	In house	375	ex	-0.54	
2138	KS M9722	326	ex	-1.20	
2169		-----		-----	
2215	In house	392.11	ex	-0.31	
2241		-----		-----	
2250	CEN-TS15968	219	ex	-2.63	
2293	CEN-TS15968	316.0	ex	-1.33	
2295		-----		-----	
2350	In house	306.56		-1.46	
2357	EN15968	435.1		0.26	
2358	CEN-TS15968	420.8		0.07	
2363	EPA3540C/8321B	406		-0.13	
2365	In house	454.77		0.52	
2366	CEN-TS15968	out capability		-----	
2375	In house	391		-0.33	
2378	CEN-TS15968	out of capability		-----	
2379	CEN-TS15968	434.247		0.25	
2384	CEN-TS15968	not applicable		-----	
2386	CEN-TS15968	224.65	ex	-2.55	
2390	CEN-TS15968	445.01		0.39	
2492	In house	168.09	ex	-3.31	
2532	CEN-TS15968	166	ex	-3.34	
2590	CEN-TS15968	357.968		-0.77	
2749		-----		-----	
2835		-----		-----	
2857	CEN-TS15968	not analyzed		-----	
2858	In house	145.00	ex	-3.62	
2892	CEN-TS15968	305.630	ex	-1.47	
2953	CEN-TS15968	235.936	ex	-2.40	
3172	CEN-TS15968	423.51	ex	0.11	
3176	CEN-TS15968	303.0	ex	-1.51	
3210	In house	306.00	ex	-1.46	
3246	CEN-TS15968	308	ex	-1.44	
3248		-----		-----	

				All participants:	
	normality	suspect		OK	
	n	11		28	
	outliers	0 (+17ex)		0	
	mean (n)	415.587		331.325	
	st.dev. (n)	48.0390	RSD = 12%	101.5465	RSD = 31%
	R(calc.)	134.509		284.330	
	st.dev.(iis)	74.8056		59.6384	
	R(iis)	209.456		166.988	
comp					
	R(Horwitz)	106.245	(2 components)	87.642	

Ex = test result excluded when Soxhlet extraction was not used, see paragraph 4.1 and 5
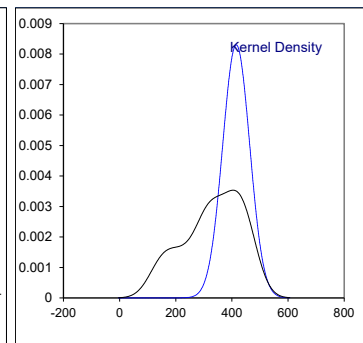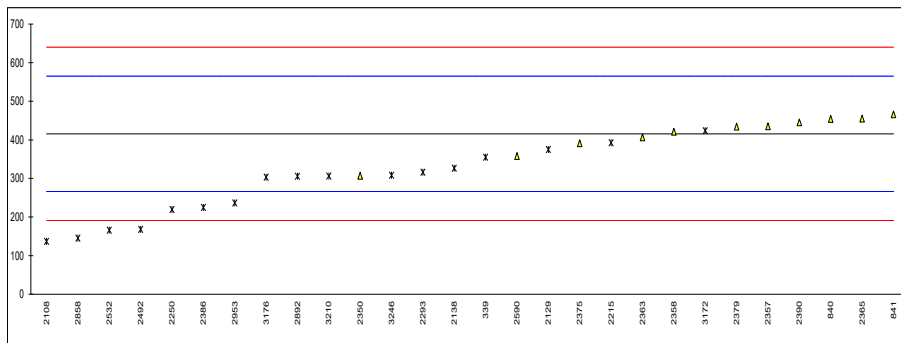
APPENDIX 2

Abbreviations of components:

PFOA	**=**	Perfluorooctanoic acid
PFOS	**=**	Perfluorooctanesulfonic acid
PFNA	**=**	Perfluorononanoic acid
PFDA	**=**	Perfluorodecanoic acid
PFBS	**=**	Perfluorobutanesulfonic acid
PFODA	**=**	Perfluorooctadecanoic acid
PFDoA	**=**	Perfluorododecanoic acid
Other	**=**	Other Per- and Polyfluorinated compound(s)

Other reported Per- & Polyfluorinated Compounds in sample #21710; results in mg/kg

lab	PFOA	PFNA	PFDA	PFBS	PFODA	PFDoA	Other
339	0.337	<1	<0,1	<0,1	<1	<1	not analyzed
551	-----	-----	-----	-----	-----	-----	-----
840	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-----
841	<0.01	<0.01	<0.01	<0.01	No capabilities	<0.01	Not applicable
2108	0.03	n.d.	n.d	n.d.	-----	n.d.	-----
2129	1.5	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
2138	-----	-----	-----	-----	-----	-----	-----
2169	0.27203	-----	-----	-----	-----	-----	64.921 *)
2215	not detected	not determined	not determined	not detected	not determined	not determined	not determined
2241	<1.0	<1.0	<1.0	-----	<1.0	<1.0	-----
2250	0.0248	-----	-----	-----	-----	-----	*)
2293	0.05	-----	-----	not detected	-----	-----	-----
2295	-----	-----	-----	-----	-----	-----	-----
2350	< 1.00	< 1.00	< 1.00	< 1.00	not applicable	< 1.00	not applicable
2357	-----	-----	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	n.d.	N/A	n.d.	N/A
2363	<1	<1	<1	<1	-----	<1	-----
2365	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0 *)
2366	<1	out capability	out capability	out capability	out capability	out capability	-----
2375	-----	-----	-----	-----	-----	-----	*)
2378	<1	out of capability	out of capability	out of capability	out of capability	out of capability	out of capability
2379	Not detected	Not detected	Not detected	Not detected	Not tested	Not detected	Not tested
2384	12.2094	not applicable	not applicable	not applicable	not applicable	not applicable	not applicable
2386	0.042	<0,02	<0,002	0.0057	<0,004	<0,002	-----
2390	Not detected	Not detected	Not detected	Not detected	Not analyzed	Not detected	41.95 *)
2492	-----	-----	-----	-----	-----	-----	-----
2532	Not Detected	Not Detected	Not Detected	Not Detected	-----	Not Detected	-----
2590	0.403	-----	-----	-----	-----	-----	*)
2749	-----	-----	-----	-----	-----	-----	-----
2835	-----	-----	-----	-----	-----	-----	-----
2857	not detected	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed
2858	0.04	not detected	not detected	not detected	not detected	not detected	not detected
2892	-----	-----	-----	-----	-----	-----	-----
2953	-----	-----	-----	-----	-----	-----	25.328
3172	< 1	< 1	< 1	< 1	< 1	< 1	-----
3176	-----	-----	-----	-----	-----	-----	*)
3210	0.057	not detected	not detected	0.095	-----	not detected	-----
3246	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed
3248	-----	-----	-----	-----	-----	-----	-----

*)
Lab 2169 reported: Perfluorohexanesulfonic acid(PFHxS) 65 mg/kg Perfluorohexanoic acid(PFHxA) 0.27mg/kg
Lab 2250 reported: PFBA: 0,0501 mg/kg; PFPeA: 0,0431 mg/kg; PFHxA: 0,0346 mg/kg; PFHpA:0,0208 mg/kg; PFHxS: 7,15 mg/kg;
　　　　PFHpS: 3,01 mg/kg
Lab 2365 reported: PFHxS:115.6 PFHpS:37.0
Lab 2375 reported: PFHxS 47 mg/kg - PFHpS 23 mg/kg
Lab 2390 reported: pfHps=42 mg/kg
Lab 2590 reported: Other PFCs detected: PFHxS = 106.61 mg/kg, PFHpS= 38.40 mg/kg
Lab 3176 reported: PFHxS (Cas No: 355-46-4) = 34,7 mg/kg PFHpS (Cas No: 375-92-8) = 35,4 mg/kg

Other reported Per- & Polyfluorinated Compounds in sample #21711; results in mg/kg

lab	PFOS	PFNA	PFDA	PFODA	PFDoA	Other
339	<0,1	<1	<1	<0,1	<0,1	<0,1
551	-----	-----	-----	-----	-----	-----
840	n.d.	n.d.	n.d.	n.d.	n.d.	-----
841	<0.01	<0.01	<0.01	No capabilities	<0.01	Not applicable
2108	n.d.	n.d.	n.d.	-----	n.d.	-----
2129	3.25	<0,01	<0,01	<0,01	<0,01	<0,01
2138	-----	-----	-----	-----	-----	-----
2169	0.01455	-----	-----	-----	-----	0.36455 *)
2215	not detected	not determined	not determined	not determined	not determined	not determined
2241	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
2250	-----	-----	-----	-----	-----	*)
2293	not detected	-----	-----	-----	-----	-----
2295	-----	-----	-----	-----	-----	-----
2350	< 1.00	< 1.00	< 1.00	N/A	< 1.00	N/A
2357	-----	-----	-----	-----	-----	-----
2358	n.d.	n.d.	n.d.	N/A	n.d.	N/A
2363	<1	<1	<1	-----	<1	-----
2365	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
2366	<1	out capability	out capability	out capability	out capability	-----
2375	-----	-----	-----	-----	-----	*)
2378	<1	out of capability	out of capability	out of capability	out of capability	out of capability
2379	Not detected	Not detected	Not detected	Not tested	Not detected	Not tested
2384	not detected	not applicable	not applicable	not applicable	not applicable	not applicable
2386	0.0076	0.011	<0,002	<0,004	<0,002	-----
2390	Not detected	Not detected	Not detected	Not analyzed	Not detected	Not detected
2492	-----	-----	-----	-----	-----	-----
2532	Not detected	Not detected	Not detected	-----	Not detected	-----
2590	0.045	-----	-----	-----	-----	-----
2749	-----	-----	-----	-----	-----	-----
2835	not detected	-----	-----	-----	-----	-----
2857	not detected	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed
2858	not detected	not detected	not detected	not detected	not detected	not detected
2892	-----	-----	-----	-----	-----	-----
2953	-----	-----	-----	-----	-----	5.09
3172	< 1	< 1	< 1	< 1	< 1	*)
3176	-----	-----	-----	-----	-----	3.83
3210	0.0076	0.11	0.0062	-----	not detected	-----
3246	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed
3248	-----	-----	-----	-----	-----	-----

*)
Lab 2169 reported: Perfluorohexanesulfonic acid(PFHxS) <0.005 mg/kg Perfluorohexanoic acid(PFHxA) 0.36 mg/kg
Lab 2250 reported: PFBA: 0,165 mg/kg; PFPeA: 0,018 mg/kg; PFHxA: 0,160 mg/kg; PFHpA: 1,55 mg/kg
Lab 2375 reported: PFHpA 2.4 mg/kg
Lab 3176 reported: Perfluoroheptanoic acids, PFHpA (Cas No : 375-85-9)

APPENDIX 3　　Analytical details

lab	Accredited ISO /IEC 17025	Sample intake (g)	Sample pre-treatment prior to analysis	Type of extraction	Solvent(s) for extraction	Time extraction (min)	Temperature extraction (°C)
339	---	---	---	---	---	---	---
551	No	0.5g	Further cut	Soxhlet	DCM:Methanol	---	---
840	Yes	0.5g	Further cut	Soxhlet	DCM:Methanol (1:1)	60 min	105°C
841	Yes	0.5 gram	Further cut	Soxhlet	DCM+Methanol	6 hrs	/
2108	Yes	0,5 g	Used as received	Ultrasonic	MeOH	1 h	60°C
2129	Yes	0,1g	Further grinded	Ultrasonic	MeOh	30 min	RT
2138	Yes	1 g	Used as received	Ultrasonic	Methanol	2 hours	60
2169	No	0.5g	Further grinded	Ultrasonic	Methanol	2 hours	60℃
2215	No	1g	Further cut	Ultrasonic	methanol	120min	60℃
2241	Yes	0.5g	Further cut	Soxhlet	DCM: Methanol=1:1	360 minutes	/
2250	Yes	0,3 g	Used as received	Ultrasonic	Methanol	120 min	60 °C
2293	Yes	0.5 grams	Further cut	Ultrasonic	Methanol	120 minutes	60 °C
2295	---	---	---	---	---	---	---
2350	Yes	0.5 g	Further cut	Soxhlet	DCM:Methanol=1:1	6hr	50
2357	Yes	---	Further cut	Soxhlet	DCM:Methanol(1:1)	6hr	/
2358	Yes	0.5 g	Further cut	Soxhlet	Methanol/DCM (1:1 V/V)	360 mins	/
2363	Yes	0.5g	Further cut	Soxhlet	DCM : MeoH=1 : 1	360 min	/
2365	Yes	0.2g	Further cut	Soxhlet	methanol : DCM =1:1	5.5hours	120℃
2366	Yes	---	Further cut	Soxhlet	---	---	---
2375	Yes	0.5 gram	Further cut	Soxhlet	Methanol:DCM (1:1)	90 min	105°C
2378	No	0.5g	Used as received	Soxhlet	methanol	600min	60
2379	No	0.5 grams	Further cut	Soxhlet	DCM : MeOH	360 minutes	100 °C
2384	Yes	0.5g	Further cut	Soxhlet	DCM and Methanol	360 minutes	30-40
2386	Yes	1	Used as received	Ultrasonic	MeOH	120	60
2390	Yes	0.5 gram	Used as received	Soxhlet	DCM: methanol (1:1)	6 hours	
2492	No	0.25 g	Used as received	Ultrasonic	MeOH	60	60
2532	Yes	0.5 grams	Further cut	Ultrasonic	Methanol:water	120 minutes	60 °C
2590	Yes	0.5 g	Further cut	Soxhlet	MeOH: DCM, 1:1	5h	not applicable
2749	---	---	---	---	---	---	---
2835	Yes	0.5g	Further cut	Stirrer	methanol	6 hours	40
2857	No	0.1g	Further grinded	Ultrasonic	Methanol	120 minutes	60°C
2858	Yes	1.00 gm	Used as received	Ultrasonic	Methanol	60	60
2892	Yes	1.0g	Further cut	Ultrasonic	Methanol	120	60
2953	Yes	0,2g	Further cut	Ultrasonic	methanol	60	60°C
3172	Yes	0.2	Further grinded	Ultrasonic	Methanol-DCM 1:1	120	60
3176	Yes	2	Used as received	Ultrasonic	methanol	120	60
3210	No	1g	Further cut	Ultrasonic	Methanol	120 minutes	60°C
3246	---	---	---	---	---	---	---
3248	---	---	---	---	---	---	---

APPENDIX 4

Number of participants per country

    1 lab in BANGLADESH

    1 lab in BRAZIL

    2 labs in FRANCE

    4 labs in GERMANY

    1 lab in GUATEMALA

    3 labs in HONG KONG

    1 lab in INDIA

    3 labs in ITALY

    1 lab in JAPAN

    1 lab in MALAYSIA

    7 labs in P.R. of CHINA

    1 lab in PAKISTAN

    1 lab in SINGAPORE

    2 labs in SOUTH KOREA

    1 lab in SWITZERLAND

    1 lab in TAIWAN

    1 lab in THAILAND

    3 labs in TURKEY

    4 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
f+?	= possibly a false positive test result?
f-?	= possibly a false negative test result?

Literature

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3.   ISO5725 parts 1-6:94
4.   ISO13528:05
5.   M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
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7.   P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
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9.   Analytical Methods Committee, Technical Brief, No 4, January 2001
10.   P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364, (2002)
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13.   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 (perfluorooctane sulfonates)
14.   Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants
15.   Commission Delegated Regulation (EU) 2020/784 of 8 April 2020 amending Annex I to Regulation (EU) 2019/1021 of the European Parliament and of the Council as regards the listing of perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds