Results of Proficiency Test Total Per- & Polyfluoroalkyl Substances (PFAS) in Polymers September 2020

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 became 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 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 2020/2021, it was decided to continue the proficiency test for the analysis of Total PFAS in Polymers.
In this interlaboratory study 40 laboratories in 21 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 of polymer labelled #20670 and #20671 of approximately 3 grams each. Both were artificially fortified on PFOS, PFOA and/or PFDoA. 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 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

For the first sample a batch of light grey PVC granulates was selected which was made positive on PFOS by a third party laboratory. After homogenization the batch was divided over 70 subsamples in small bags of 3 gram each and labelled #20670. The homogeneity of the subsamples was checked by determination of the Total PFOS content according to an in-house test method on eight stratified randomly selected subsamples. Total means the sum of linear and branched isomers per type of PFAS.

	Total PFOS in mg/kg
sample #20670-1	404
sample #20670-2	403
sample #20670-3	406
sample #20670-4	396
sample #20670-5	418
sample #20670-6	388
sample #20670-7	406
sample #20670-8	411

Table 1: homogeneity test results of subsamples #20670

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)	25
reference method	iis PTs, see paragraph 4.1
0.3 x R (reference method)	61

Table 2: evaluation of the repeatability of subsamples #20670

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 orange PVC rings was selected which was made positive on PFOA and PFDoA (Polyfluorododecanoic Acid) by a third party laboratory. After homogenization the batch was divided over 70 subsamples in small bags of 3 gram each and labelled #20671. The homogeneity of the subsamples was checked by determination of the Total PFOA and Total PFDoA content according to an in-house test method on nine stratified randomly selected subsamples. Total means the sum of linear and branched isomers per type of PFAS.

	Total PFOA in mg/kg	Total PFDoA in mg/kg
sample #20671-1	311	310
sample #20671-2	311	309
sample #20671-3	318	316
sample #20671-4	305	311
sample #20671-5	330	331
sample #20671-6	304	323
sample #20671-7	298	308
sample #20671-8	311	325
sample #20671-9	315	323

Table 3: homogeneity test results of subsamples #20671

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 PFDoA in mg/kg
r (observed)	26	23
reference method	iis PTs, see paragraph 4.1	iis PTs, see paragraph 4.1
0.3 x R (reference method)	47	48

Table 4: evaluation of the repeatabilities of subsamples #20671

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 a set of 1 subsample #20670 and 1 subsample #20671 was sent on August 12, 2020.

2.5 ANALYZES

The participants were requested to determine on samples #20670 and #20671 the total of each individual PFAS: Perfluorooctanoic acid (PFOA), Perfluorooctanesulfonic acid (PFOS), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), Perfluorobutanesulfonic acid (PFBS), Perfluorooctadecanoic acid (PFODA) and to report other Per- and Polyfluorinated substances. Also, some analytical details were requested to be reported. Only after the PT was closed, test results for Perfluorododecanoic acid (PFDoA) were requested for sample #20671 (see paragraph 5). 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 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:

	$\lvert z\rvert < 1$	good
$1 <$	$\lvert z\rvert < 2$	satisfactory
$2 <$	$\lvert z\rvert < 3$	questionable
$3 <$	$\lvert z\rvert$	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. One participant reported test results after the PT was closed, referencing difficulties due to COVID-19. Four participants did not report any test results and not all participants were able to report all components requested.
Finally, 36 reporting laboratories submitted 88 numerical test results. Observed were 5 outlying test results, which is 5.7%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

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

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 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.
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 the other PFAS. 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 for more discussion also paragraph 5 and appendix 1.

Sample #20670

Total PFOS: This determination was problematic. Two statistical outliers were observed and seventeen 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 Proficiency Tests.

NB: Total means the sum of linear and branched isomers per type of PFAS.

The majority of the participants agreed on a concentration near or below the limit of detection for the other Per- & Polyfluorinated substances. The material had not been spiked with these components. Therefore, it was decided not to calculate z-scores for these determinations. The reported test results are given in appendix 2.

Sample #20671

Total PFOA: This determination was problematic. Two statistical outliers were observed and sixteen 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 Proficiency Tests.

Total PFDoA: This determination was problematic. One statistical outlier was observed and seven 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 Proficiency Tests. See also paragraph 5 for more discussion.

NB: Total means the sum of linear and branched isomers per type of PFAS.

The majority of the participants agreed on a concentration near or below the limit of detection for the other Per- & Polyfluorinated substances. The material had not been spiked with these components. 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 estimated from previous iis PTs 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 derived from previous iis PTs are presented in the next table.

Component	unit	n	average	2.8 * sd	R(target)
Total PFOS	mg/kg	17	332	251	167

Table 5: reproducibility of test on samples #20670

Component	unit	n	average	2.8 * sd	R(target)
Total PFOA	mg/kg	17	210	131	106
Total PFDoA	mg/kg	9	188	162	95

Table 6: reproducibilities of tests on samples #20671

Without further statistical calculations, it can be concluded that there is not a good compliance of the group of participating laboratories with the target reproducibilities. The problematic tests have been discussed in paragraph 4.1.

4.3 COMPARISON OF PROFICIENCY TEST OF SEPTEMBER 2020 WITH PREVIOUS PTS

	September 2020	August 2019	September 2018	September 2017	September 2016
Number of reporting laboratories	36	27	32	35	48
Number of test results	88	130	118	119	162
Number of statistical outliers	5	7	1	10	10
Percentage of statistical outliers	5.7%	5.4%	0.8%	8.4%	5.8%

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	2020	2019	2018	2017	2016 -2012	iis Target
Total PFOS	27%	18-21%	22%	13-24%	19-24%	18%
Total PFOA	22%	20%	21%	20%	18-30%	18%
Total PFNA	n.d.	n.d.	34%	n.d.	n.d.	18%
Total PFBS	n.d.	26%	n.d.	n.d.	n.d.	18%
Total PFDoA	31%	n.d.	n.d.	n.d.	n.d.	18%

Table 8: development of relative uncertainties over the years

The uncertainties observed in this PT for PFOA and PFOS are larger than the uncertainties in previous PTs. The uncertainty of PFDoA is a new component in this PT.

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 (n=36) the following can be summarized:

- 26 participants (≈70%) reported to be accredited for this test 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 10 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=19) and one other group (n=16) that used Ultrasonic for extraction. One laboratory used Mechanical Shaking.
- 32 participants mentioned to have used Methanol in combination with or without Dichloromethane or Toluene as extraction solvent. One participant mentioned to have used only Dichloromethane and another used Acetone.
- 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

After the PT was closed it was observed that the expected PFODA (Polyfluorooctadecanoic Acid) was not present in both samples, but a number of participants reported in the comments to have found PFDoA (Polyfluorododecanoic Acid) in sample #20671. After investigation it was found that indeed in the homogeneity tests the component PFDoA was found, but due to a mix-up of the letters of the abbreviation of this component, it was reported as PFODA. With this finding iis sent out a report form for the reporting of PFDoA in sample #20671 and seventeen participants reported a test result for PFDoA. Therefore, it was decided to evaluate this component in appendix 1.

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 below for an example

for the PFOS component in sample #20670 and PFOA in sample #20671. 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.

Analytical Details	Sample	unit	n	average	2.8 * sd	RSD (%)
Ultrasonic extraction PFOS	#20670	mg/kg	16	182	458	90
Soxhlet extraction PFOS	#20670	mg/kg	17	332	251	27
Ultrasonic extraction PFOA	#20671	mg/kg	16	78	218	100
Soxhlet extraction PFOA	#20671	mg/kg	17	210	131	22

Table 9: reproducibility of PFOS and PFOA with different extraction methods in polymers

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.

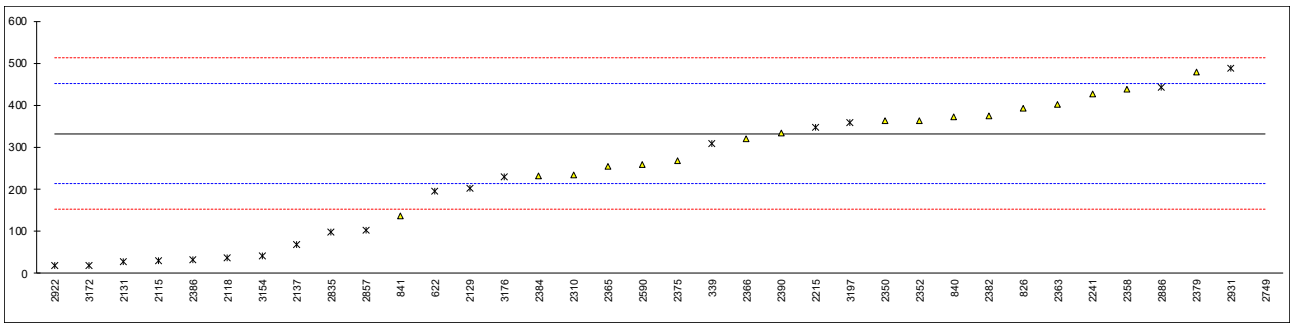
APPENDIX 1

Determination of PFOS (Polyfluorooctanesulfonic Acid) on sample #20670; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		-----		-----	
339	In house	308	ex	-0.41	
622	CEN-TS15968	196.35	ex	-2.27	
826	CEN-TS15968	392.9		1.01	
840	CEN-TS15968	372		0.67	
841	CEN-TS15968	135.97		-3.28	
2115	CEN-TS15968	30.1	ex	-5.05	
2118	In house	36.43	ex	-4.95	
2129	CEN-TS15968	202	ex	-2.18	
2131	In house	27.66351	ex	-5.09	
2137	KS M9722	69.19	ex	-4.40	
2215	CEN-TS15968	347	ex	0.25	
2241	CEN-TS15968	426.42		1.58	
2310	CEN-TS15968	235		-1.63	
2350	In house	363.02		0.51	
2352	In house	363.5		0.52	
2357		-----		-----	
2358	CEN-TS15968	436.8		1.75	
2363	In house	402.2		1.17	
2365	In house	255.15		-1.29	
2366	CEN-TS15968	319.4		-0.21	
2375	CEN-TS15968	268		-1.07	
2379	CEN-TS15968	478.90		2.45	
2382	CEN-TS15968	375.0		0.72	
2384	CEN-TS15968	231.9493		-1.68	
2386	CEN-TS15968	31.265	ex	-5.03	
2390	CEN-TS15968	333.16		0.02	
2590	CEN-TS15968	258.5200		-1.23	
2749	In house	4273	ex	65.90	
2835	In house	98.685	DG(0.05)	-3.91	
2857	CEN-TS15968	103	ex	-3.83	
2886	In house	443	ex	1.85	
2922	CEN-TS15968	18.579	ex	-5.24	
2931	In house	487.04	ex	2.59	
3154	CEN-TS15968	42.244	DG(0.05)	-4.85	
3163		not analysed		-----	
3172	CEN-TS15968	18.6325	ex	-5.24	
3176	In house	228.4	ex	-1.74	
3197	CEN-TS15968	358.8	ex	0.44	
3210		-----		-----	

					<u>All participants:</u>
	normality	OK			OK
	n	17			35
	outliers	2 (+17 ex)			1
	mean (n)	332.229			248.408
	st.dev. (n)	89.7655	RSD = 27%		152.0616 RSD = 61%
	R(calc.)	251.343			425.773
	st.dev.(iis)	59.8012			44.7134
	R(iis)	167.443			125.197
Compare					
	R(Horwitz)	107.587	(3 components)		84.042

ex = test result excluded when Soxhlet extraction was not used, see paragraph 4.1 and 5.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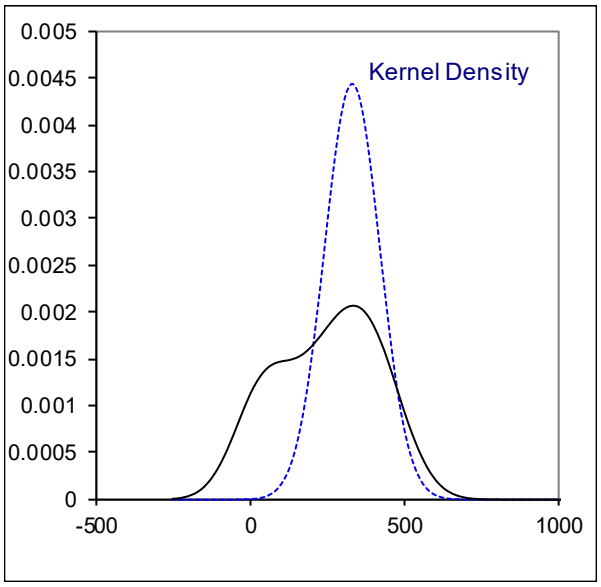
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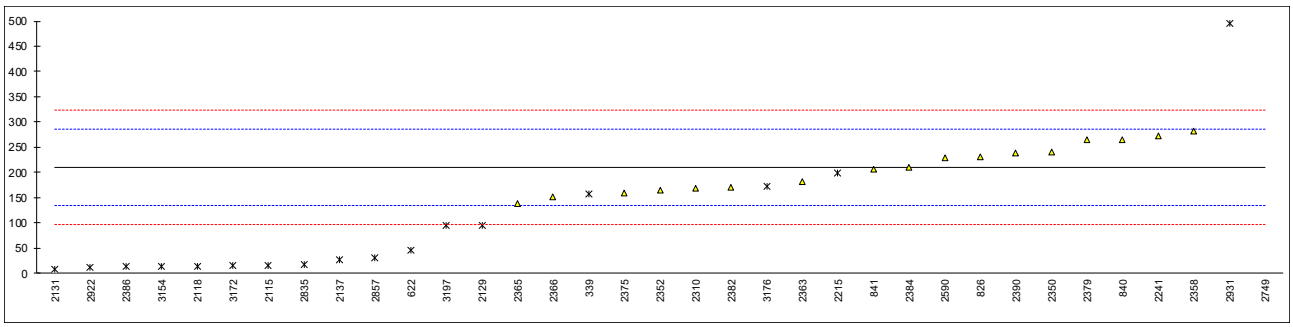
0
500
1000

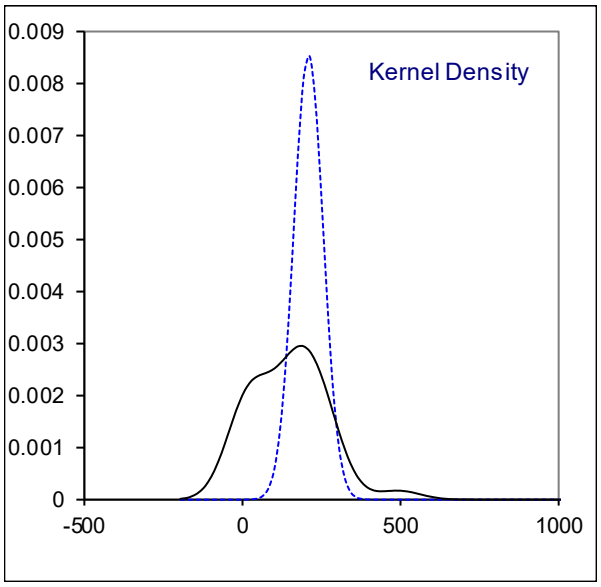
Determination of PFOA (Polyfluorooctanoic Acid) on sample #20671; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		-----		-----	
339	In house	157	ex	-1.41	
622	CEN-TS15968	45.34	ex	-4.36	
826	CEN-TS15968	231.3		0.56	
840	CEN-TS15968	264		1.42	
841	CEN-TS15968	205.37		-0.13	
2115	CEN-TS15968	15.21	ex	-5.15	
2118	In house	13.70	ex	-5.19	
2129	CEN-TS15968	94.8	ex	-3.05	
2131	In house	8.32455	ex	-5.34	
2137	KS M9722	25.90	ex	-4.87	
2215	CEN-TS15968	198	ex	-0.32	
2241	CEN-TS15968	273.24		1.67	
2310	CEN-TS15968	169		-1.09	
2350	In house	240.97		0.81	
2352	In house	165.0		-1.19	
2357		-----		-----	
2358	CEN-TS15968	282.02		1.90	
2363	In house	182.4		-0.73	
2365	In house	137.65		-1.92	
2366	CEN-TS15968	151.8		-1.54	
2375	CEN-TS15968	159		-1.35	
2379	CEN-TS15968	263.90		1.42	
2382	CEN-TS15968	170.0		-1.06	
2384	CEN-TS15968	210.2023		0.00	
2386	CEN-TS15968	13.27	ex	-5.20	
2390	CEN-TS15968	237.98		0.74	
2590	CEN-TS15968	228.7308		0.49	
2749	In house	4336	ex	109.07	
2835	In house	17.935	DG(0.05)	-5.08	
2857	CEN-TS15968	31	ex	-4.74	
2886		-----		-----	
2922	CEN-TS15968	11.794	ex	-5.24	
2931	In house	495.64	ex	7.55	
3154	CEN-TS15968	13.592	DG(0.05)	-5.20	
3163		not analysed		-----	
3172	CEN-TS15968	14.5538	ex	-5.17	
3176	In house	173.0	ex	-0.98	
3197	CEN-TS15968	94.6	ex	-3.05	
3210		-----		-----	

				All participants
	normality	OK		suspect
	n	17		34
	outliers	2 (+16 ex)		1
	mean (n)	210.151		146.948
	st.dev. (n)	46.6808	RSD = 22%	112.0126 RSD = 76%
	R(calc.)	130.706		313.635
	st.dev.(iis)	37.8271		26.4506
	R(iis)	105.916		74.062
	R(Horwitz)	59.317	(2 components)	43.930

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


500
450
400
350
300
250
200
150
100
50
0
2131
2922
2386
3154
2118
3172
2115
2835
2137
2857
622
3197
2129
2365
2366
339
2375
2352
2310
2382
3176
2363
2215
841
2384
2590
826
2390
2350
2379
840
2241
2358
2931
2749

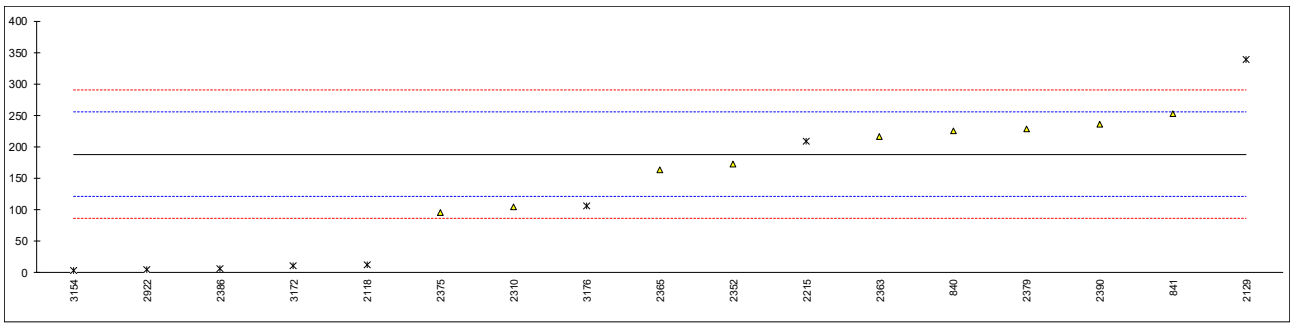

Kernel Density
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
-500
0
500
1000

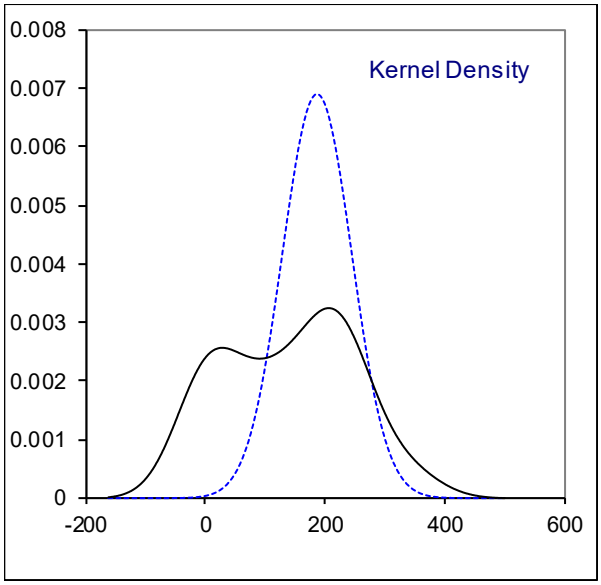
Determination of PFDoA (Polyfluorododecanoic Acid) on sample #20671; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110		-----		-----	
339		-----		-----	
622		-----		-----	
826		-----		-----	
840	CEN-TS15968	226.0		1.11	
841	CEN-TS15968	253		1.91	
2115		-----		-----	
2118	In house	12.50	ex	-5.19	
2129	CEN-TS15968	339	ex	4.44	
2131		-----		-----	
2137		-----		-----	
2215	CEN-TS15968	209.34	ex	0.62	
2241		-----		-----	
2310	CEN-TS15968	105		-2.46	
2350		-----		-----	
2352	In house	172		-0.48	
2357		-----		-----	
2358		-----		-----	
2363	In house	215.8		0.81	
2365	In house	163.76		-0.73	
2366		-----		-----	
2375	CEN-TS15968	95		-2.75	
2379	CEN-TS15968	228.61		1.19	
2382		-----		-----	
2384		-----		-----	
2386	CEN-TS15968	6.499	ex	-5.36	
2390	CEN-TS15968	236.05		1.41	
2590		-----		-----	
2749		-----		-----	
2835		-----		-----	
2857		-----		-----	
2886		-----		-----	
2922	CEN-TS15968	4.374	ex	-5.43	
2931		-----		-----	
3154	CEN-TS15968	2.981	G(0.05)	-5.47	
3163		-----		-----	
3172	CEN-TS15968	11.3174	ex	-5.22	
3176	In house	106.0	ex	-2.43	
3197		-----		-----	
3210		-----		-----	

				All participants:
	normality	OK		OK
	n	9		17
	outliers	1 (+7ex)		0
	mean (n)	188.358		140.425
	st.dev. (n)	57.8578	RSD = 31%	106.4175 RSD = 76%
	R(calc.)	162.002		297.969
	st.dev.(iis)	33.9044		33.9044
	R(iis)	94.932		70.774
Compare				
	R(Horwitz)	54.245	(2 components)	42.268

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


400
350
300
250
200
150
100
50
0
3154
2922
2386
3172
2118
2375
2310
3176
2365
2352
2215
2363
840
2379
2390
841
2129


Kernel Density
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
-200
0
200
400
600

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 #20670; results in mg/kg

lab	PFOA	PFNA	PFDA	PFBS	PFODA	Other
110	-----	-----	-----	-----	-----	-----
339	0.101	<0.02	<0.02	-----	-----	-----
622	0.37	-----	-----	-----	-----	-----
826	-----	-----	-----	-----	-----	-----
840	not detected	not detected	not detected	not detected	not detected	not applicable
841	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
2115	0.027	-----	-----	0.0076	-----	13.99
2118	0.02	not detected	not detected	0.01	not analysed	8.82
2129	0.153	-----	-----	-----	-----	-----
2131	0.016575	0	0	0	-----	-----
2137	-----	-----	-----	-----	-----	-----
2215	not detected	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed
2241	<2.5	<2.5	<2.5	not analyzed	not analyzed	not analyzed
2310	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	*)
2350	< 1.00	< 1.00	< 1.00	< 1.00	N/A	N/A
2352	0.203	-----	-----	-----	-----	-----
2357	-----	-----	-----	-----	-----	-----
2358	not detected	not detected	not detected	not detected	not applicable	not applicable
2363	<1.0	<1.0	<1.0	<1.0	NA	NA
2365	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
2366	<1	out cap	out cap	out cap	out cap	out cap
2375	-----	-----	-----	-----	-----	-----
2379	Not detected	Not detected	Not detected	Not detected	Not detected	-----
2382	＜1.0	＜1.0	＜1.0	＜1.0	＜1.0	＜1.0
2384	Not Detected	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable
2386	0.024	<0,01	<0,01	<0,01	Not Analysed	6.606
2390	not detected	not detected	not detected	not detected	not detected	not detected
2590	0.1836	not detected	not detected	0.0452	not detected	-----
2749	0.129	-----	-----	-----	-----	-----
2835	Not Detected	Not Analysed	Not Analysed	Not Analysed	Not Analysed	Not Analysed
2857	not determined	not analysed	not analysed	not analysed	not analysed	not analysed
2886	-----	-----	-----	-----	-----	-----
2922	0.02012	not detected	not detected	0.0039002	not analysed	not analysed
2931	0.324	not detected	not detected	0.02	not detected	43.19
3154	0.030	-----	-----	0.005	-----	**)
3163	not analysed	not analysed	not analysed	not analysed	not analysed	-----
3172	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	4.29
3176	-----	-----	-----	-----	-----	-----
3197	-----	-----	-----	-----	-----	-----
3210	-----	-----	-----	-----	-----	-----

*) lab 2310: PFHXS= 47.4mg/kg, PFHPS=15.8mg/kg
**) lab 3154: 5,860 PFHxS; 0,033 PFPeA; 0,030 PFHxA; 0,020 PFHpA

Other reported Per- & Polyfluorinated Compounds in sample #20671; results in mg/kg

lab	PFOS	PFNA	PFDA	PFBS	PFODA	Other
110	-----	-----	-----	-----	-----	-----
339	0.717	0.0968	0.0782	-----	-----	-----
622	0.46	-----	-----	-----	-----	-----
826	-----	-----	-----	-----	-----	-----
840	not detected	not detected	not detected	not detected	not detected	not applicable
841	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
2115	0.047	0.0065	0.0059	-----	15.65	0.445
2118	0.05	not detected	not detected	not detected	not analysed	0.38
2129	0.322	-----	-----	-----	-----	-----
2131	0.02585	0	0	0	-----	-----
2137	-----	-----	-----	-----	-----	-----
2215	not detected	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed
2241	<2.5	<2.5	<2.5	not analyzed	not analyzed	not analyzed
2310	NOT DETECTED	NOT DETECTED	NOT DETECTED	NOT DETECTED	-----	*)
2350	< 1.00	< 1.00	< 1.00	< 1.00	N/A	N/A
2352	0.647	-----	-----	-----	-----	-----
2357	-----	-----	-----	-----	-----	-----
2358	not detected	not detected	not detected	not detected	not applicable	not applicable
2363	<1.0	<1.0	<1.0	<1.0	NA	NA
2365	<1.0	<1.0	<1.0	<1.0	-----	163.76
2366	<1	out cap	out cap	out cap	out cap	out cap
2375	-----	-----	-----	-----	-----	-----
2379	0.96	Not detected	Not detected	Not detected	not detected	-----
2382	＜1.0	＜1.0	＜1.0	＜1.0	＜1.0	180.0
2384	Not Detected	Not Applicable	Not Applicable	Not Applicable	Not Applicable	Not Applicable
2386	0.035	<0,01	<0,01	<0,01	Not Analysed	0.228
2390	not detected	not detected	not detected	not detected	-----	not detected
2590	0.7427	0.0536	0.0534	not detected	223.3654	-----
2749	0.932	-----	-----	-----	-----	-----
2835	Not Detected	Not Analysed	Not Analysed	Not Analysed	Not Analysed	Not Analysed
2857	not determined	not analysed	not analysed	not analysed	not analysed	not analysed
2886	0.143	-----	-----	-----	-----	-----
2922	0.0280996	0.0031337	0.0029644	not detected	not analysed	not analysed
2931	0.91	0.14	0.16	0.18	not detected	56.97
3154	0.129	0.00345	0.0026	-----	-----	**)
3163	not analysed	not analysed	not analysed	not analysed	not analysed	not analysed
3172	< 0.5	< 0.5	< 0.5	< 0.5	-----	-----
3176	-----	-----	-----	-----	-----	-----
3197	-----	-----	-----	-----	-----	-----
3210	-----	-----	-----	-----	-----	-----

*) Lab 2310: PFBA 0.91 and FFHPA 1.5
**) Lab 3154: 0,0039 PFPeA; 0,0292 PFHxA; 0,219 PFHpA

APPENDIX 3 Analytical details

lab	Accredited acc. to ISO /IEC17025	Sample intake (g)	Sample pre-treatment prior to analysis	Type of extraction	Solvent(s) for extraction	Time extraction (min)	Temperature extraction (°C)
110	---		---	---			
339	No	0.5	Further cut	Ultrasonic	Methanol/Toluene	120	30
622	Yes	1	Further cut	Ultrasonic	Methanol LC grade	2 hours	60 °C
826	No	0.5 g	Further grinded	Soxhlet	Methanol/DCM (1/1)	360	
840	Yes	0.5G	Further cut	Soxhlet	methanol/dichloromethane (1:1)	1h	105
841	Yes	0.5007	Further cut	Soxhlet	Dichloromethane	6 hours	
2115	Yes	1 g	Used as received	Ultrasonic	MeOH	2 h	60°C
2118	No	0.5	Used as received	Ultrasonic	methanol	60	60 °C
2129	Yes	0,5	Further grinded	Ultrasonic	Methanol	30 min	70°C
2131	Yes	1	Used as received	Ultrasonic	Methanol	60	60
2137	No	1	Used as received	Ultrasonic	Methanol	2 hr	60
2215	Yes	1	Further cut	Ultrasonic	methanol	120min	60℃
2241	Yes	0.2	Further cut	Soxhlet	DCM: MEOH (1:1)	360	/
2310	Yes	0.5	Used as received	Soxhlet	Dicholormethane:Methanol(1:1V/V)	6 hours	70
2350	Yes	0.5	Further cut	Soxhlet	DCM:Methanol=1:1	6hr	50°C
2352	Yes	0.5	Further cut	Soxhlet	Methanol:dichlormethane=1:1	6h	
2357	---		---	---			
2358	Yes	0.5	Further cut	Soxhlet	DCM : Methanol(1:1)	360 min	N/A
2363	Yes	0.5	Further cut	Soxhlet	MeOH:DCM=1:1	6 hours	80°C
2365	Yes	0.5	Further cut	Soxhlet	Dichloromethane:methanol=1:1	2h	120°C
2366	No	0.5	Further cut	Soxhlet	methanol: DCM =1:1	6h	/
2375	Yes	0,5	Further cut	Soxhlet	MeOH:DCM (1:1)	90 Min	105 C
2379	No	0.5	20670 As received 20671 Further cut	Soxhlet	DCM : MeOH 1 : 1	360 min	100 °C
2382	Yes	0.5	Further cut	Soxhlet	MEOH:DCM=1 : 1	6h	/
2384	Yes	0.5	Further cut	Soxhlet	Dichloromethane and Methanol	360 min	30 - 40
2386	Yes	1	Used as received	Ultrasonic	Methanol	120	60
2390	Yes	0.5	Further cut	Soxhlet	Methanol: dichloromethane	360 min	N/A
2590	No	0.5	Used as received	Soxhlet	DCM:MEOH 1:1	360 min	Not applic.
2749	No	0.2	Used as received	Mechanical Shaking	Aceton, 2 h swell	10 min. shaking	room temp.
2835	Yes	0.1g	Further cut	Soxhlet	Methanol	2 hours	40 °C
2857	Yes	0.01-0.03	Further cut	Ultrasonic	Methanol	2H	60°C
2886	No	1	Further cut	Ultrasonic	Methanol	120	60
2922	Yes	1	Used as received	Ultrasonic	Methanol	2 hours	60°C
2931	No		Further grinded	Ultrasonic			
3154	Yes	0,5	Used as received	Soxhlet			
3163	No	x	---	---	x	x	x
3172	Yes	1.5	Further cut	Ultrasonic	Methanol	120	60
3176	Yes	1	Further cut	Ultrasonic	MeOH	120	60
3197	Yes	0,5 g	Further cut	Ultrasonic	Methanol	120 min.	60
3210	---		---	---			

APPENDIX 4

Number of participants per country

1 lab in	AUSTRIA
1 lab in	BELGIUM
1 lab in	DENMARK
2 labs in	FRANCE
4 labs in	GERMANY
1 lab in	HONG KONG
1 lab in	INDIA
1 lab in	INDONESIA
3 labs in	ITALY
1 lab in	MALAYSIA
8 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	SINGAPORE
3 labs in	SOUTH KOREA
2 labs in	SWITZERLAND
1 lab in	TAIWAN
1 lab in	THAILAND
1 lab in	THE NETHERLANDS
3 labs 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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