Institute for
Interlaboratory Studies

Results of Proficiency Test Total Per- and Polyfluoroalkyl Substances (PFAS) in Polymers September 2022

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 (iis) organizes a proficiency scheme for the determination of Total Per- and Polyfluoroalkyl Substances (PFAS) in polymers every year. During the annual proficiency testing program 2022/2023 it was decided to continue the proficiency test for the determination of Total PFAS in Polymers.

In this interlaboratory study 28 laboratories in 15 countries registered for participation, see appendix 4 for the number of participants per country. In this report the results of the Total PFAS in Polymers 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 analyzes for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory.
It was decided to send two different samples made of PVC of approximately 3 grams each labelled #22710 and #22711 respectively.
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 brown PVC blocks was selected which was artificially fortified with PFOS. After homogenization 60 small plastic bags were filled with approximately 3 grams each and labelled #22710.
The homogeneity of the subsamples was checked by the determination of Total PFOS content using an in house test method on 8 stratified randomly selected subsamples.

	Total PFOS in mg/kg
sample #22710-1	597.1
sample #22710-2	607.9
sample #22710-3	571.9
sample #22710-4	568.6
sample #22710-5	590.9
sample #22710-6	586.6
sample #22710-7	610.9
sample #22710-8	576.9

Table 1: homogeneity test results of subsamples #22710

From the above test results the repeatability was calculated and compared with 0.3 times the estimated reproducibility calculated from average PT uncertainties of previous iis 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)	44.5
reference method	iis PTs
0.3 x R (reference method)	89.0

Table 2: evaluation of the repeatability of subsamples #22710

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

For the second sample a batch of pink PVC blocks fortified with PFOS and PFOA was selected. After homogenization 60 small plastic bags were filled with approximately 3 grams each and labelled #22711.
The homogeneity of the subsamples was checked by determination of Total PFOS and Total PFOA content using an in house test method on eight stratified randomly selected subsamples.

	Total PFOS in mg/kg	Total PFOA in mg/kg
sample #22711-1	2009	2561
sample #22711-2	1958	2377
sample #22711-3	1979	2475
sample #22711-4	2120	2676
sample #22711-5	2061	2660
sample #22711-6	2012	2516
sample #22711-7	2129	2532
sample #22711-8	1926	2430

Table 3: homogeneity test results of subsamples #22711

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

	Total PFOS in mg/kg	Total PFOA in mg/kg
r (observed)	206	291
reference method	iis PTs	iis PTs
0.3 x R (reference method)	306	382

Table 4: evaluation of the repeatabilities of subsamples #22711

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

To each of the participating laboratories two PVC samples labelled #22710 and #22711 were sent on August 24, 2022.

2.5 ANALYZES

The participants were requested to determine on both samples #22710 and #22711 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. Total means the sum of linear and branched isomers per type of PFAS.
It was also requested to report if the laboratory was accredited for the determined components and to report some analytical details.

It was explicitly requested to treat the samples as if they were routine samples and to report the test results using the indicated units on the report form and not to round the test results, but 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 appendices 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 appendices 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 (derived from 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 were 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:

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

The $z_{(target)}$ scores are listed in the test result tables in appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. Therefore, the usual interpretation of z-scores is as follows:

	|z|	< 1	good
1 <	|z|	< 2	satisfactory
2 <	|z|	< 3	questionable
3 <	|z|		unsatisfactory

4 EVALUATION

In this proficiency test no problems were encountered with the dispatch of the samples. Two participants reported test results after the final reporting date and four other participants did not report any test results. Not all participants were able to report all tests requested. In total 24 participants reported 72 numerical test results. Observed were 8 outlying test results, which is 11.1%. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

All data sets proved to have a normal Gaussian distribution.

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 and used 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 iis PTs of 2018 till 2021 this RSD has been confirmed which means that 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. See for more discussion paragraph 5.

sample #22710

Total PFOS: This determination was not problematic. Five statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the estimated reproducibility obtained from previous iis proficiency tests.

The majority of the participants agreed on a concentration near or below the limit of detection for the other PFAS mentioned in paragraph 2.5. Therefore, no z-scores are calculated. The test results are given in appendix 2.

sample #22711

Total PFOA: This determination was problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated reproducibility obtained from previous iis proficiency tests.

Total PFOS: This determination was not problematic. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is in agreement with the estimated reproducibility obtained from previous iis proficiency tests.

The majority of the participants agreed on a concentration near or below the limit of detection for the other PFAS mentioned in paragraph 2.5. Therefore, no z-scores are calculated. The 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 derived from reference methods are presented in the next table.

Component	unit	n	average	2.8 * sd	R(target)
Total PFOS	mg/kg	19	557	204	281

Table 5: reproducibility of test on sample #22710

Component	unit	n	average	2.8 * sd	R(target)
Total PFOA	mg/kg	23	1400	871	706
Total PFOS	mg/kg	22	1293	443	652

Table 6: reproducibilities of tests on sample #22711

Without further statistical calculations it can be concluded that there is a good compliance of the group of participants with the target reproducibilities for PFOS in both samples.

4.3 COMPARISON OF PROFICIENCY TEST OF SEPTEMBER 2022 WITH PREVIOUS PTS

	September 2022	September 2021	September 2020	August 2019	September 2018
Number of reporting laboratories	24	36	36	27	32
Number of test results	72	98	88	130	118
Number of statistical outliers	8	2	5	7	1
Percentage of statistical outliers	11.1%	2.0%	5.7%	5.4%	0.8%

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 test was compared to uncertainties observed in PTs over the years, expressed as relative standard deviation (RSD) of the PTs, see next table.

Component	September 2022	September 2021	September 2020	August 2019	2018 -2012	Target
Total PFOS	12-13%	19%	27%	18-21%	19-24%	18%
Total PFOA	22%	16%	22%	20%	18-30%	18%
Total PFNA	--	--	--	--	34%	18%
Total PFBS	--	12%	--	26%	--	18%
Total PFDoA	--	--	31%	--	--	18%

Table 8: development of the uncertainties over the years

In comparison with previous iis PTs it is observed that the performance of the group improved for Total PFOS. The uncertainty for Total PFOA is in line with previous iis PTs.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

Seventeen participants (74%) reported to be ISO/IEC17025 accredited for the determination of Per- and Polyfluoroalkyl Substances in polymers.

For this proficiency test some analytical details were requested, see appendix 3 for the reported details. Based on the answers given by the participants the following can be summarized:

- 16 participants have further cut/grinded the samples before use and 7 participants have used the samples as received.
- 2 participants used between 0.05 and 0.1 grams as sample intake, 13 participants used 0.5 grams and 6 participants used 1 gram as sample intake.
- regarding the extraction technique 12 participants have used Soxhlet and 8 participants used the Ultrasonic method. One laboratory used Mechanical Shaking and one other laboratory reported Thermal Desorption.
- 18 participants used Methanol in combination with or without Dichloromethane as extraction solvent. One participant used Methanol/Toluene and one other participant used Methanol in combination with THF. The use of only THF was reported by one participant.
- the participants that used Soxhlet extraction all used an extraction time of 6 hours at a temperature between 30-105 °C, while the extraction time used by the Ultrasonic participants was mostly 2 hours and sometimes 1 hour at a temperature of 60 °C. One participant mentioned to have used Mechanical Shaking with an extraction time of 16 hours at 20 °C.

The effect of the extraction technique on the determination was further discussed in paragraph 5.

5 DISCUSSION

In this PT, the average of the homogeneity test results for sample #22711 are not in line with the average (consensus value) from the PT results. There are several reasons for this. First, the goal of the homogeneity testing is very different from the goal of the evaluation of the reported PT results. In order to prove the homogeneity of the PT samples, a test method is selected with a high precision (smallest variation). The accuracy (trueness) of the test method is less relevant.
Secondly, the homogeneity testing is done by one laboratory only. The test results of this (ISO/IEC 17025 accredited) laboratory will have a bias (systematic deviation) depending on the test method used. The desire to detect small variations between the PT samples leads to the use of a sensitive test method with high precision, which may be a test method with significant bias.
Also each test result reported by the laboratories that participate in the PT will have a bias. However, some will have a positive bias and others a negative bias. These different biases compensate each other in the PT average (consensus value). Therefore, the PT consensus value may deviate from the average of the homogeneity test. At the same time the accuracy of the PT consensus value is more reliable than the accuracy of the average of the results of the homogeneity test.

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 of PFAS from polymers. For polymers CEN/TS15968 method refers to ISO6427 and to ISO9113. In test method ISO6427 table 1 and 2 several extraction methods dependent on the type of polymers are listed. In ISO6427 it is recommended to use Soxhlet for extraction of PFAS from PVC samples.
In previous iis PTs participants that did not use Soxhlet extraction for PVC polymers were excluded from the statistical evaluation to get a good estimation of the consensus value of the components present in PT samples. In this 2022 PT the effect of the extraction technique used has also been investigated. For sample #22710 the Ultrasonic extraction technique in combination with Methanol as solvent yields lower levels PFOS for four participants. In the statistical analysis these test results were marked as outliers. Remarkably, the effect of the use of different extraction techniques in combination of different extraction solutions was not visible in the test results. Therefore, it was decided not to exclude data from the statistical analysis based on extraction technique.

In this report “total” means the sum of linear and branched isomers per type of PFAS. In previous iis 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

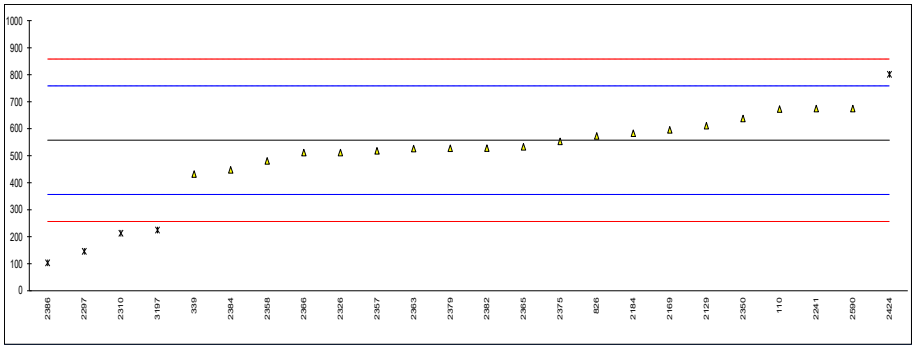
Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

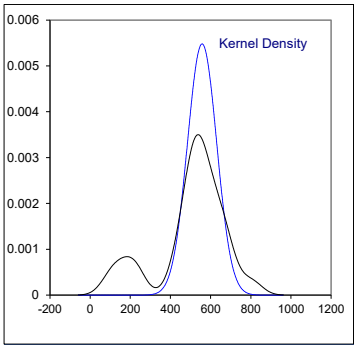
APPENDIX 1

Determination of Total PFOS (Perfluorooctanesulfonic acid) on sample #22710; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	CEN-TS15968	673		1.15	
339	In house	432		-1.25	
826	CEN-TS15968	573		0.16	
2129	In house	611		0.53	
2169	CEN-TS15968	595.6		0.38	
2184	CEN-TS15968	583.18	C	0.26	first reported 103.53
2241	CEN-TS15968	674.40		1.17	
2293		-----		-----	
2297	ISO23702	145.7	C,R(0.01)	-4.10	first reported 82.6
2310	CEN-TS15968	213	R(0.01)	-3.43	
2326	CEN-TS15968	511.35		-0.46	
2350	CEN-TS15968	637.9		0.80	
2357	CEN-TS15968	518.1		-0.39	
2358	CEN-TS15968	480.53		-0.77	
2363	In house	526		-0.31	
2365	In house	532.541		-0.25	
2366	CEN-TS15968	511		-0.46	
2375	In house	553		-0.04	
2379	CEN-TS15968	527.529		-0.30	
2382	CEN-TS15968	528.1		-0.29	
2384	CEN-TS15968	447.89		-1.09	
2386	CEN-TS15968	103.182	R(0.01)	-4.53	
2424	In house	800.94	C,R(0.01)	2.43	first reported 960.96
2590	In house	674.6	C	1.17	first reported 1792.186
2916		-----		-----	
3163		-----		-----	
3197	CEN-TS15968	224.8	C,R(0.01)	-3.32	first reported 106.680
3210		-----		-----	

	normality	OK	
	n	19	
	outliers	5	
	mean (n)	557.406	
	st.dev. (n)	72.7734	RSD = 13%
	R(calc.)	203.765	
	st.dev.(iis)	100.3331	
	R(iis)	280.933	
compare			
	R(Horwitz)	166.982	(3 components)

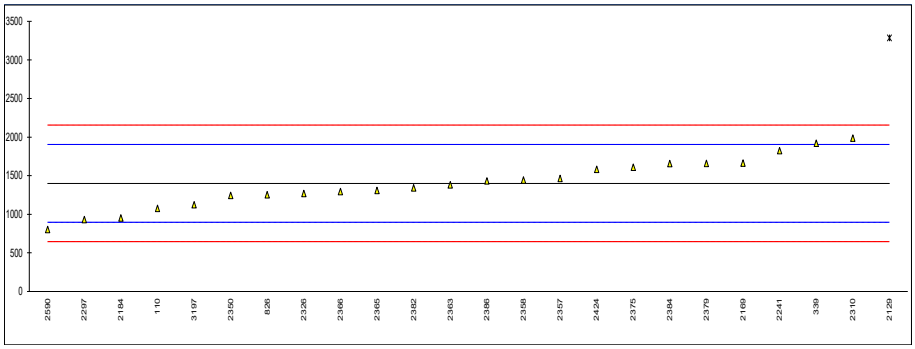


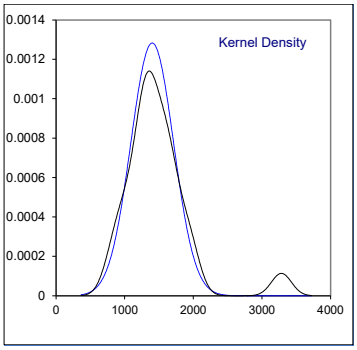


Determination of Total PFOA (Perfluorooctanoic acid) on sample #22711; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	CEN-TS15968	1077		-1.28	
339	In house	1920		2.06	
826	CEN-TS15968	1251		-0.59	
2129	In house	3284	R(0.01)	7.47	
2169	CEN-TS15968	1662.2		1.04	
2184		950.43		-1.78	
2241	CEN-TS15968	1822.71		1.68	
2293		-----		-----	
2297	ISO23702	930.8		-1.86	
2310	CEN-TS15968	1987		2.33	
2326	CEN-TS15968	1268.24		-0.52	
2350	CEN-TS15968	1243.9		-0.62	
2357	CEN-TS15968	1464.3		0.25	
2358	CEN-TS15968	1443.23		0.17	
2363	In house	1382		-0.07	
2365	In house	1309.184		-0.36	
2366	CEN-TS15968	1294		-0.42	
2375	In house	1609		0.83	
2379	CEN-TS15968	1657.011		1.02	
2382	CEN-TS15968	1341.5		-0.23	
2384	CEN-TS15968	1656.81		1.02	
2386	CEN-TS15968	1432		0.13	
2424	In house	1580.85	C	0.72	first reported 8188.9
2590	In house	800.875		-2.38	
2916		-----		-----	
3163		-----		-----	
3197	CEN-TS15968	1122.07		-1.10	
3210		-----		-----	

	normality	OK	
	n	23	
	outliers	1	
	mean (n)	1400.266	
	st.dev. (n)	310.9930	RSD = 22%
	R(calc.)	870.780	
	st.dev.(iis)	252.0478	
	R(iis)	705.734	
Compare			
	R(Horwitz)	298.162	(2 components)

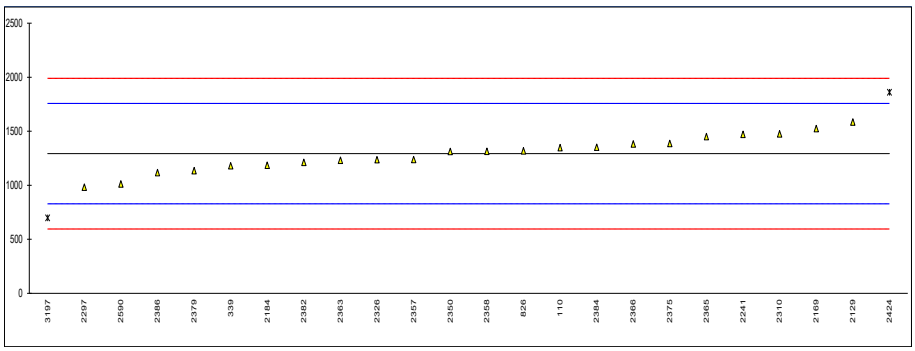


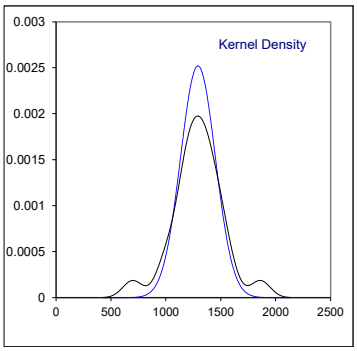


Determination of Total PFOS (Perfluorooctanesulfonic acid) on sample #22711; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	CEN-TS15968	1348		0.24	
339	In house	1180		-0.49	
826	CEN-TS15968	1318		0.11	
2129	In house	1585		1.25	
2169	CEN-TS15968	1524.2		0.99	
2184		1186.09		-0.46	
2241	CEN-TS15968	1471.61		0.77	
2293		-----		-----	
2297	ISO23702	982.6		-1.33	
2310	CEN-TS15968	1476		0.79	
2326	CEN-TS15968	1236.28		-0.24	
2350	CEN-TS15968	1312.4		0.08	
2357	CEN-TS15968	1238.2		-0.24	
2358	CEN-TS15968	1313.58		0.09	
2363	In house	1230		-0.27	
2365	In house	1449.557		0.67	
2366	CEN-TS15968	1382		0.38	
2375	In house	1387		0.40	
2379	CEN-TS15968	1134.972		-0.68	
2382	CEN-TS15968	1211.3		-0.35	
2384	CEN-TS15968	1351.51		0.25	
2386	CEN-TS15968	1116		-0.76	
2424	In house	1861.55	C,R(0.05)	2.44	first reported 2291.1
2590	In house	1011.187		-1.21	
2916		-----		-----	
3163		-----		-----	
3197	CEN-TS15968	698.14	R(0.05)	-2.56	
3210		-----		-----	

	normality	OK	
	n	22	
	outliers	2	
	mean (n)	1292.977	
	st.dev. (n)	158.3215	RSD = 12%
	R(calc.)	443.300	
	st.dev.(iis)	232.7358	
	R(iis)	651.660	
compare			
	R(Horwitz)	341.262	(3 components)





APPENDIX 2

Abbreviations of components:

PFOA = Perfluorooctanoic acid
PFNA = Perfluorononanoic acid
PFDA = Perfluorodecanoic acid
PFBS = Perfluorobutanesulfonic acid
PFODA = Perfluorooctadecanoic acid
PFDoA = Perfluorododecanoic acid
Other = Other Per- and Polyfluorinated Substances

Other reported Per- and Polyfluoroalkyl Substances in sample #22710; results in mg/kg

lab	PFOA	PFNA	PFDA	PFBS	PFODA	PFDoA	Other *)
110	not detected	not detected	not detected	not detected	not detected	not detected	not detected
339	1.74	<1	<1	<1	<1	<1	<1
826	-----	-----	-----	-----	-----	-----	-----
2129	0.8995	<0,01	<0,01	<0,01	<0,01	<0,01	See below
2169	0.243	-----	-----	-----	-----	-----	68.9 *)
2184	0.11	< RL	< RL	< RL	< RL	< RL	15.26 *)
2241	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	-----
2293	-----	-----	-----	-----	-----	-----	-----
2297	0.064	Not detected	Not detected	Not detected	Not detected	Not detected	Not Determined
2310	not detected	not detected	not detected	not detected	not analyzed	not detected	See below
2326	not detected	not detected	not detected	not detected	not detected	Not Capable	Not detected
2350	Not detected	Not detected	Not detected	Not detected	Not analyzed	Not detected	Not analyzed
2357	0.28	-----	-----	-----	-----	-----	-----
2358	0.313	not detected	not detected	not detected	not detected	not detected	not detected
2363	0.25	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
2365	0.243	＜0.010	＜0.010	＜0.010	＜0.010	＜0.010	＜0.010
2366	<1	out capability	out capability	out capability	out capability	out capability	-----
2375	-----	-----	-----	-----	-----	-----	See below
2379	Not detected	Not detected	Not detected	Not detected	Not Analyzed	Not detected	Not Analyzed
2382	＜0.5	＜0.5	＜0.5	＜0.5	＜0.5	＜0.5	＜0.5
2384	Not detected	-----	-----	-----	-----	-----	-----
2386	0.0749	< 0,02	< 0,02	< 0,02	not analyzed	< 0,04	not analyzed
2424	0.0310	not detected	not detected	0.0372	-----	not detected	-----
2590	0.589	0.017	-----	0.076	-----	-----	-----
2916	-----	-----	-----	-----	-----	-----	-----
3163	-----	-----	-----	-----	-----	-----	-----
3197	0.096	-----	-----	0.023	-----	-----	-----
3210	-----	-----	-----	-----	-----	-----	-----

*)
Lab 2129 reported: PFBA:1,6 mg/kg, PFPeA:1,4 mg/kg, PFHxA:0,98 mg/kg, PFHpA:0,67, DONA: 0,74 mg/kg, PFHxS:76 mg/kg, PFHpS:25 mg/kg, PFPrA:4,1 mg/kg
Lab 2169 reported: Other Perfluorohexanesulfonic acid
Lab 2184 reported: other substance = PFHxS (15.26 mg/kg)
Lab 2310 reported: PFHxS- 31mg/kg, PFHpS- 17mg/kg
Lab 2375 reported: PFHxS 87 mg/kg, PFHpS 37 mg/kg

Other reported Per- and Polyfluoroalkyl Substances in sample #22711; results in mg/kg

lab	PFNA	PFDA	PFBS	PFODA	PFDoA	Other *)
110	not detected	not detected	not detected	not detected	not detected	not detected
339	<1	<1	<1	<1	<1	<1
826	-----	-----	-----	-----	-----	-----
2129	<0,01	<0,01	<0,01	-----	<0,01	See below
2169	-----	-----	-----	-----	-----	171.3 *)
2184	-----	-----	-----	-----	-----	126.60 *)
2241	<1.0	<1.0	<1.0	<1.0	<1.0	-----
2293	-----	-----	-----	-----	-----	-----
2297	Not detected	Not detected	Not detected	Not detected	Not detected	Not Determined
2310	not detected	not detected	not detected	not analyzed	not detected	See below
2326	not detected	not detected	not detected	not detetected	Not Capable	Not detected
2350	Not detected	Not detected	Not detected	Not analyzed	Not detected	Not analyzed
2357	-----	-----	-----	-----	-----	-----
2358	not detected	not detected	not detected	not detected	not detected	not detected
2363	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
2365	＜0.010	＜0.010	＜0.010	＜0.010	＜0.010	＜0.010
2366	out capability	out capability	out capability	out capability	out capability	-----
2375	-----	-----	-----	-----	-----	See below
2379	Not detected	Not detected	Not detected	Not Analyzed	Not detected	Not Analyzed
2382	＜0.5	＜0.5	＜0.5	＜0.5	＜0.5	No capacity
2384	-----	-----	-----	-----	-----	-----
2386	< 0,2	< 0,2	< 0,2	not analyzed	< 0,4	not analyzed
2424	not detected	not detected	0.0407	-----	not detected	-----
2590	-----	-----	0.215	-----	-----	-----
2916	-----	-----	-----	-----	-----	-----
3163	-----	-----	-----	-----	-----	-----
3197	-----	-----	-----	-----	-----	-----
3210	-----	-----	-----	-----	-----	-----

*)
Lab 2129 reported: PFPrA:33 mg/kg, PFHpS: 79 mg/kg, PFHxS: 201 mg/kg, DONA: 9,5 mg/kg, PFHpA:39 mg/kg, PFPeA: 8,4 mg/kg, PFBA:12 mg/kg
Lab 2169 reported: Other Perfluorohexanesulfonic acid
Lab 2184 reported: other substance = PFHxS (126.60 mg/kg)
Lab 2310 reported: PFHxS- 163mg/kg, PFHpS- 95.6mg/kg, PFHxA- 5.49mg/kg, PFHpA- 22.3mg/kg, PFBA- 2.05mg/kg
Lab 2375 reported: PFHxA 3,4 mg/kg PFHxS 190 mg/kg PFHpA 23 mg/kg PFHpS 89 mg/kg

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)	Temp. extraction (°C)
110	Yes	0.5 g	Further grinded	Soxhlet	Methanol/DCM (1:1 v/v)	360 min	60°C
339	No	1g	Used as received	Ultrasonic	MeOH/toluene (50/50)	2h	60°C
826	No	0.1 g	Further grinded	Soxhlet	MeOH:DCM (1:1)	360	70
2129	No	---	cryogenic grinding	Mechanical Shaking	Methanol	16h	20C
2169	Yes	1 g	Further grinded	Ultrasonic	Methanol	120 min	60 ℃
2184	No	---	Used as received	Thermal Desorption	---	---	---
2241	Yes	0.5g	Further cut	Soxhlet	DCM:Methanol=1:1	360 min	/
2293	---	---	---	---	---	---	---
2297	Yes	1	Used as received	Ultrasonic	Methanol	60	60
2310	Yes	1	Used as received	Ultrasonic	Methanol	120	60
2326	Yes	0.5 g	Further cut	Soxhlet	Methanol/DCM 1:1	6 hour	55°C
2350	Yes	0.5g	Further cut	Soxhlet	Methanol/DCM 1:1	6 hours	N/A
2357	---	---	---	---	---	---	---
2358	Yes	0.5g	Further cut	Soxhlet	DCM/Methanol 1:1	360 min	
2363	Yes	0.5 g	Further cut	Soxhlet	DCM:MeOH=1:1	6 h	
2365	Yes	0.5g	Further cut	Ultrasonic	THF:methanol=1:1	120min	60℃
2366	Yes	0.5g	Further grinded	Soxhlet	---	---	---
2375	Yes	0,5 g	Further cut	Soxhlet	MeOH:DCM (1:1)	6 hours	105 °C
2379	No	0.5 g	Further cut	Soxhlet	Methanol : DCM	360 min	100 C
2382	Yes	1g	Further cut	Ultrasonic	MEOH	2h	60℃
2384	Yes	0.5g	Further cut	Soxhlet	DCM and methanol (1:1)	360 min	30-40
2386	Yes	1	Used as received	Ultrasonic	Methanol	120	60
2424	No	0.05-0.1	Used as received	Ultrasonic	THF	60	60
2590	Yes	0.5g	Used as received	Soxhlet	MeOH	---	---
2916	---	---	---	---	---	---	---
3163	---	---	---	---	---	---	---
3197	Yes	0,5	Further cut	Ultrasonic	Methanol	120	60
3210	---	---	---	---	---	---	---

APPENDIX 4

Number of participants per country

2 labs in FRANCE
3 labs in GERMANY
1 lab in GUATEMALA
2 labs in HONG KONG
1 lab in INDIA
1 lab in ITALY
1 lab in JAPAN
2 labs in KOREA, Republic of
1 lab in MALAYSIA
7 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in THAILAND
1 lab in THE NETHERLANDS
2 labs in TURKEY
2 labs in U.S.A.

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
E = calculation difference between reported test result and result calculated by iis
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
fr. = first reported
f+? = possibly a false positive test result?
f-? = possibly a false negative test result?

Literature

1. iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
2. ISO5725:86
3. ISO5725 parts 1-6:94
4. ISO13528:05
5. M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
6. W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
7. P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
8. J.N. Miller, Analyst, 118, 455, (1993)
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)
11. W. Horwitz and R. Albert, J. AOAC Int, 79.3, 589-621, (1996)
12. Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), 165-172, (1983)
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