Results of Proficiency Test Per-&Polyfluorinated Compounds in polymer, total September 2017

Organised by: Institute for Interlaboratory Studies
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1 INTRODUCTION

Perfluorooctanoic acid (PFOA) is one important representative of the substance group of per- and polyfluorinated substances. The hazard profile of PFOA is well known: PFOA is a persistent, bio-accumulative, and toxic substance, which may cause severe and irreversible adverse effects on the environment and human health. PFOA was the first PFC (Poly/Per Fluorinated Chemicals) to be identified as substance of very high concern (SVHC) under REACH by unanimous agreement between EU Member States in 2014. Besides PFOA also other fluorinated substances have properties of concern, which are targeted by the following international regulations: Perfluorinated carboxylic acids with a carbon chain of eleven to fourteen carbon atoms (PFBS, PFHxS, PFHxA, PFOS, PFNA, PFDA, 8:2 FTOH) are listed as SVHC on the REACH candidate list because of their persistent and bio-accumulative properties. Perfluoro-octane sulfonic acid (PFOS) is listed as persistent organic pollutant (POP) in Annex B of the Stockholm Convention.
To protect health and environment, the European Union promulgated Directive 2006/122/EC on 27 December 2006, in which the placing on the market and the use of per- and polyfluorinated substances is restricted: “Semi-finished products or articles, or parts thereof, if the concentration of PFOS/PFOA is equal or greater than 0.1% by mass” and “May not be placed on the market or used as a substance or constituent of preparations in a concentration equal to or higher than 0.005 % by mass.”

On request of several participants, the Institute for Interlaboratory Studies decided to organise an interlaboratory study for the determination of PFOA and PFOS content in the 2012 PT program. This PT was continued each following year. In the interlaboratory study of September 2017, 38 laboratories from 18 different countries registered for participation (See appendix 3). In this report, the results of the 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 organiser of this proficiency test. Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. It was decided to send 2 different plastic samples (approximately 3 gram each), positive (artificially fortified) on PFOA and/or PFOS and labelled #17610 and #17611 respectively. Participants were requested to report rounded and unrounded test results and some details of the test methods used. The unrounded test results were preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in accordance with ISO/IEC 17043:2010 (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 organisation 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 March 2017 (iis-protocol, version 3.4). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

2.4 SAMPLES

Two different PVC samples, #17610 artificially fortified to be positive on PFOA and PFOS and #17611 artificially fortified on PFOA, were selected. The materials were divided over 100 plastic bags, approx. 3 grams for each sample.

The homogeneity of the subsamples of #17610 was checked by determination of PFOA and PFOS content on eight stratified randomly selected subsamples of #17610.

	PFOA in mg/kg	*PFOS in mg/kg*
sample #17610-1	2561	2009
sample #17610-2	2377	1958
sample #17610-3	2475	1979
sample #17610-4	2676	2120
sample #17610-5	2660	2061
sample #17610-6	2516	2012
sample #17610-7	2532	2129
sample #17610-8	2430	1926

Table 1: homogeneity test results of subsamples #17610

From the above test results of the homogeneity tests, the relative between sample standard deviations $\%RSD_r$ were calculated and compared with 0.3 times the relative proficiency test target standard deviations RSD_R of 2016 (iis16P09) in agreement with the procedure of ISO 13528, Annex B2 in table 2 below.

	PFOA	*PFOS*
RSD_r (observed)	4.1%	3.6%
reference	Horwitz	Horwitz
0.3 x %Horwitz	2.1% (2 comp)	2.6% (3 comp)
reference	iis16P09	iis16P09
0.3 x RSD_R (iis16P09)	5.4%	5.7%

Table 2: relative repeatability standard deviations of PFOA/PFOS contents of the subsamples #17610

The homogeneity of the subsamples of #17611 was checked by determination of PFOS content on eight stratified randomly selected subsamples of #17611.

	PFOS in mg/kg
sample #17611-1	366.5
sample #17611-2	368.4
sample #17611-3	350.0
sample #17611-4	366.6
sample #17611-5	366.1
sample #17611-6	353.1
sample #17611-7	348.4
sample #17611-8	358.0

Table 3: homogeneity test results of subsamples #17611

From the above test results of the homogeneity tests, the relative between sample standard deviations $\%RSD_r$ were calculated and compared with 0.3 times the relative standard deviation estimated on the Horwitz equation based on three components (see also paragraph 4) in agreement with the procedure of ISO 13528, Annex B2 in table 2 below.

	PFOS
RSD_r (observed)	2.3%
reference	Horwitz
0.3 x %Horwitz	3.4% (3 comp)

Table 4: relative repeatability standard deviation of PFOS contents of the subsamples #17611

The calculated variation coefficients RSDr for sample #17610 are lower than 0.3 times the estimated reference reproducibilities using the reproducibilities observed in previous PT iis16P09 (see table 6 for an overview of the observed uncertainties over the years). The calculated variation coefficient RSDr for sample #17611 is lower than 0.3 times the estimated reference reproducibility based on the Horwitz equation. Therefore, homogeneity of all subsamples was assumed.

To each of the participating laboratories one set of samples; 1 times sample #17610 and 1 times sample #17611 was sent on August 9, 2017.

2.5 ANALYSES

The participants were requested to determine PFOA and PFOS content on both samples. It was explicitly requested to treat the samples as routine samples and to report the analytical results using the indicated units on the report form in the data entry portal and not to round the results, but report as much significant figures as possible. It was also requested not to report ‘less than’ results, which are above the detection limit, because such results can not be used for meaningful statistical calculations.

To get comparable test results a detailed report form and a letter of instructions are prepared. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories were also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.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 sample and per component in the appendix 1 of this report. The laboratories are represented by their code numbers.

Directly after the deadline, a reminder was sent to those laboratories that did not report 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 reanalyses). Additional or corrected test results are used for the data analysis and the original test results are placed under 'Remarks' in the test result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

3.1 STATISTICS

The protocol followed in the organisation 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 March 2017 (iis-protocol, version 3.4).

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.

In accordance to ISO 5725 the original test results per determination were submitted subsequently 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. When the uncertainty passed the evaluation, no remarks are made in the report. However, when the uncertainty failed the evaluation it is mentioned in the report and it will have significant consequences for the evaluation of the test results.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

3.2 GRAPHICS

In order to visualise the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported test results are plotted. The corresponding laboratory numbers are on the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected reference test method. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.
Furthermore, Kernel Density Graphs were made. 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 literature reproducibility by division with 2.8. In general, when no literature reproducibility is available, another target may be 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 should be done in order to evaluate whether the reported test results are fit-for-purpose.

The z-scores were calculated in accordance with:

$z_{(target)}$ = (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:

	$\lvert z \rvert < 1$	good
$1 <$	$\lvert z \rvert < 2$	satisfactory
$2 <$	$\lvert z \rvert < 3$	questionable
$3 <$	$\lvert z \rvert$	unsatisfactory

4 EVALUATION

In this interlaboratory study, no problems were encountered with the dispatch of the samples. Two participants reported test results after the final reporting date and three other participants did not report any test result at all. Finally, the 35 reporting laboratories reported 119 numerical results. Observed were 10 outlying test results, which is 8.4%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

For the determination of PFOA/PFOS, the CEN-TS 15968 method may be considered to be the official EC test method by the majority of the participating laboratories. However, the scope of this method is for extractable/migratable PFOS and not for total PFOS content, see also the discussion in paragraph 4.3. Also, the CEN-TS 15968 method does not mention reproducibility requirements. Therefore, the target requirements in this study were estimated using the Horwitz equation.

About 69% of the participants reported to have used the CEN-TS 15968 method for the determination of PFOA/PFOS and about 25% an ‘in house’ test method. Another two participants reported to have used EPA3540C or EPA3550C test method. No effect of the test method used was observed on the determination of PFOA/PFOS.

In the 2017 PT on PFOA/PFOS in textile (iis17A05) it became clear that both components have branched and linear isomers. Therefore, more data were collected over the amount of linear, branched and total PFOA/PFOS. Next to this data also the chromatograms were

collected from the participating laboratories. Based on the chromatograms the Horwitz equation were calculated based on 2 components for PFOA (in general two peaks were visible in the chromatograms) and on 3 components for PFOS (in general three peaks were visible). The investigation of the effect of branched, linear and total on the reproducibility is discussed in paragraph 5. The evaluation in paragraph 4.1 is based on the original test results as reported in the Data Entry Tool. Test results and the statistical evaluation are given in appendix 1.

The three original data sets proved to have a normal Gaussian distribution. These are referred to as “OK”.

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this paragraph, the test results are discussed per sample and per test.

The test results of one participant were excluded as the used sample pre-treatment conditions were very different compared to the group. See for more discussion paragraph 4.3.

#17610:PFOA Severe analytical problems were observed in determining the PFOA concentration at a level of 1746 mg/kg. The reported PFOA concentration varies over a large range from 388 to 2456 mg/kg. One statistical outlier was observed and one another test result was excluded. The calculated reproducibility after rejection of the suspect data is not at all in agreement with the estimated reproducibility calculated using the Horwitz equation based on two components.

#17610:PFOS Analytical problems were observed in determining the PFOS concentration at a level of 1356 mg/kg. The reported PFOS concentration varies over a range from 491 to 2300 mg/kg. Four statistical outliers were observed and one another test result was excluded. The calculated reproducibility after rejection of the suspect data is not in agreement with the estimated reproducibility calculated using the Horwitz equation based on three components.

#17611: PFOA: All reporting participants agreed on a concentration lower than 10 mg/kg. The majority reported n.d. or lower than 1 mg/kg.
The material had not been spiked with PFOA. Therefore, it was decided not to calculate z-scores for this determination.

#17611:PFOS: Severe analytical problems were observed in determining the PFOS concentration at a level of 249 mg/kg. The reported PFOS concentration varies over a large range from 23 to 358 mg/kg. Five statistical outliers were observed and one another test result was excluded. The calculated reproducibility after rejection of the suspect data is not at all in agreement with the estimated reproducibility calculated using the Horwitz equation based on three components.

4.2 PERFORMANCE EVALUATION OF THE GROUP OF LABORATORIES

The calculated reproducibilities and the target reproducibilities derived from the literature, here Horwitz, based on all received test results, are compared in below table.

	unit	n	Average	2.8 * sd	R(Horwitz)
PFOA in #17610	mg/kg	33	1746	956	360
PFOS in #17610	mg/kg	30	1359	479	356
PFOA in #17611	mg/kg	23	<10	n.a.	n.a.
PFOS in #17611	mg/kg	29	249	166	84

Table 5: performance overview for the test results on samples #17610 and #17611

Without further statistical calculations, it can be concluded that there is no good compliance of the group of participating laboratories with the target reproducibilities.

Sample #17611 was earlier used in the PT of 2015 as sample #15154. Then the assigned value was 261 mg/kg PFOS which corresponds very well with the current assigned value of 249 mg/kg PFOS.

4.3 COMPARISON OF PROFICIENCY TEST OF SEPTEMBER 2017 AGAINST PREVIOUS PTS

The observed variation expressed as the relative standard deviation RSD of the test results in the 2017 PT was in line compared to the observations in previous PTs, see below table.

RSD%	*2017*	*2016 *)*	*2015 *)*	*2014 *)*	*2011 - 2013*	*Target Horwitz 100-2000 mg/kg*
PFOA	20%	18%	n.d.	144%	15-30%	7 - 11% **)
PFOS	13-24%	11-19%[a]	24[s] - 61%[a]	27[s] - 128%[a]	141-162%	9 - 14% **)

Table 6: development of uncertainties, reported as RSD, over **all (a)** or over **subset (s)** of results against previous PTs.

*) See respective published PT reports on www.iisnl.com for the explanation about the subsets

**) Horwitz estimation based on 2 components for PFOA and 3 components for PFOS

For PFOA/PFOS the target value for the precision of the PFOA and PFOS content determination in polymers was based on the Horwitz equation. These target values of 7 - 11% based on 2 components (PFOA) and 9-14% based on 3 components appears to be very optimistic. Based on the performance in this proficiency test a value lower than 20% for the variation coefficient is more feasible when participants use an effective method for sample pre-treatment and extraction (see also paragraph 4.3).

4.4 EVALUATION OF THE ANALYTICAL DETAILS

The reported details of the methods that were used by the participants are listed in appendix 2. It was decided to study only on sample #17611 the effect of the pre-treatment of the granulate on the PFOA/PFOS determination because the performance graph (see appendix 1) clearly shows that the determination of PFOS is difficult for a group of the participants.

About 72% reported to be accredited for the determination of PFOA/PFOS and 25% reported not to be accredited. However, no effect was observed on the determination of PFOS in sample #17611.

Participants that mentioned to have used the granulate ‘as received’ or ‘cut’ reported on average similar and lower values for PFOS (respectively a mean of 248 and 244 mg/kg) in sample #17611 in comparison to the group that reported to have grinded the granulate before use (a mean of 277 mg/kg). The relative variation over the test results in the group ‘grinded’ (RSD_R=12%) was also smaller than ‘cut’ (RSD_R=23%) or ‘used as received’ (RSD_R=35%).

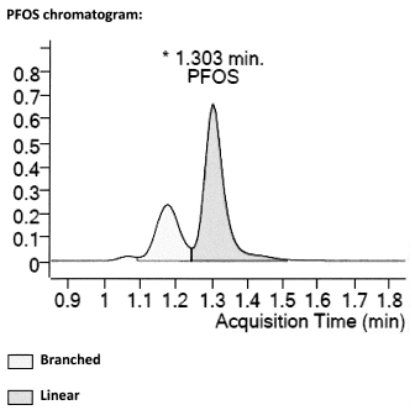
The group of participants that reported to have used for the PFOA/PFOS extraction Soxhlet with MeOH/DCM reported on average higher results (mean 268 RSD_R=17%) compared to the group that reported to have used an Ultrasonic bath with MeOH (mean 240 RSD_R=25%). The variation in the “Soxhlet” group is thus smaller.

The effect of extraction time and extraction temperature is less profound as long the time and temperature is above 10 minutes and room temperature. Therefore, the test results of one laboratory were excluded.

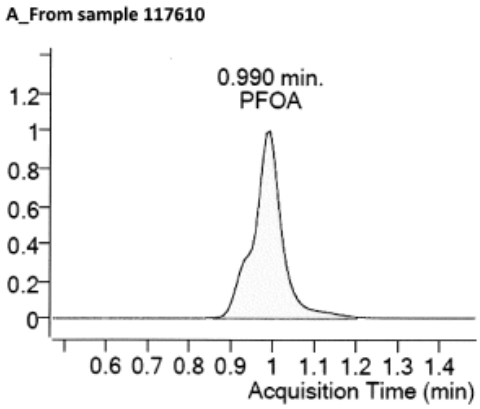
5 DISCUSSION

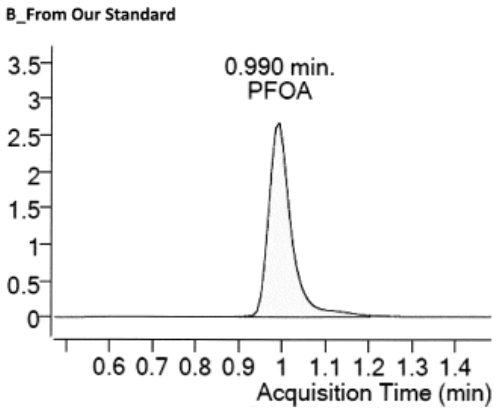
PFOA/PFOS exist in branched and linear isomers. In legislation and in the limits set to PFOA/PFOS it is not explicitly described whether **total** PFOA/PFOS (sum of branched and linear isomers) are meant. In the open literature (see for example lit 16) is explained that branched PFOA/PFOS have similar hazard profiles as the linear isomers. Therefore, it is assumed that most probably total PFOA or total PFOS are meant.
Test method CEN/TS 15968 mentions the existence of linear and branched isomers and the possibility to separate these isomers. Also it is mentioned that branched isomers have to be calculated using the response factor of the linear isomer. But method CEN/TS 15968 is not clear whether the sum of linear and branched isomers should be reported.

However, from the received chromatograms and by the extra information given it became clear that the way of integration and the way of identification of PFOA/PFOS peaks could be done in various ways.
Also the received chromatograms show different forms. Sometimes the branched isomers were totally separated from the linear peak (see right image of PFOS in sample #17610; an example of one of the participating laboratories). Sometimes no separation between branched and linear isomers was visible. In this latter case, the total surface is a measure for the sum of branched and linear isomers of PFOA or PFOS.



And sometimes only a shoulder was visible (see for example right image A of sample #17610). The surface could be integrated differently; for example, the total surface or only a part of the surface of the linear peak (particularly when the shoulder becomes more and more a peak).





Some participants are convinced that linear PFOA or PFOS were determined because the used standards are linear according to the supplier's information (see for example the image of an PFAO standard B, left). Obviously, this cannot be the case for samples #17610 and #17611 because the PFOA/PFOS used to prepare the samples turned out to be a mixture of branched and linear isomers (about 25 % branched / 75% linear).

In the reported test results (as listed in appendix 1 and summarised in table 5) some reported test results are the sum of linear and branched PFOA/PFOS (called 'total') while other reported test results may be the linear component only. Obviously, the latter only in case of a complete separation of branched and linear isomers as explained above. This difference (linear only or total) will give an extra contribution in the observed reproducibility.

	unit	n	Average	2.8 * sd	R(Horwitz)
PFOA in #17610	mg/kg	33	1746	956	360
- Total	mg/kg	19	1813	976	371
- Linear	*mg/kg*	*14*	*1455*	*854*	*218*
- Branched	*mg/kg*	*5*	*400*	*330*	*73*
PFOS in #17610	mg/kg	30	1359	479	356
- Total	mg/kg	19	1357	478	355
- Linear	*mg/kg*	*13*	*1175*	*860*	*182*
- Branched	*mg/kg*	*5*	*419*	*327*	*107*
PFOA in #17611	mg/kg	23	<10	n.a.	n.a.
- Total	mg/kg	14	<10	n.a.	n.a.
- Linear	*mg/kg*	*11*	*<10*	*n.a.*	*n.a.*
- Branched	*mg/kg*	*4*	*<10*	*n.a.*	*n.a.*
PFOS in #17611	mg/kg	29	249	166	84
- Total	mg/kg	18	255	186	86
- Linear	*mg/kg*	*10*	*214*	*173*	*43*
- Branched	*mg/kg*	*7*	*54*	*89*	*19*

Table 7: performance overview for all received test results on samples #17610

Remarkably, when the ‘totals’, defined as the combination of the chromatograms and the extra input from the participants, were compared to the mean results from appendix 1/table 5 (see overview in table 7,) the means and calculated reproducibility (called 2.8 * sd) are approximately the same (for example PFOS in sample #17610 (1359 *vs* 1357 mg/kg) and 479 *vs* 478 mg/kg). Because it was not entirely the same group (for example PFOS as published in table 5 is based on 30 test results and ‘total’ PFOS in table 7 on only 19 test results) it can be concluded that the effect of a mix-up of linear or total reported PFOA/PFOS on the reproducibility is smaller than other sources of variation, e.g. the way how the sample is pre-treated and PFOA/PFOS is extracted.

Please note that the sum of ‘branched’ and ‘linear’ as listed in table 7 is not equal to the ‘total’ amount, see for example PFOS in sample #17610 (branched 419 mg/kg + linear 1175 mg/kg is not equal to 1357 mg/kg). This can be explained by the difference in interpretation of the chromatograms as discussed above. Also by the effect that some participants mentioned normally not to report branched and linear separately. It is expected that this will contribute in high uncertainties in the determined amounts of the branched and linear isomers.

6 CONCLUSION

The conclusion is that many of the participants may be able to determine PFOA and PFOS in the polymer matrix, but still a large variation is found between participant’s test results. This variation obviously is dependent on the chosen sample pre-treatment and extraction procedure. Not surprisingly, the determination of PFOA and PFOS becomes more reproducible when sample pre-treatments are chosen that releases PFOA and PFOS more effectively from the polymer. Such a pathway could be grinding the polymer prior the extraction. Then the polymer matrix is more reduced to small particles, which increases the contact surface and facilitates the release of PFOA and PFOS from the matrix.
However, one should realize that for the determination of the amount of migrated PFOA/PFOS the polymer material should probably best be treated “as received” and grinding may be not appropriate.

The presence of a mixture of branched and linear isomers of PFOA/PFOS and the problems with the identification of these groups of isomers do not explain the observed large variation.

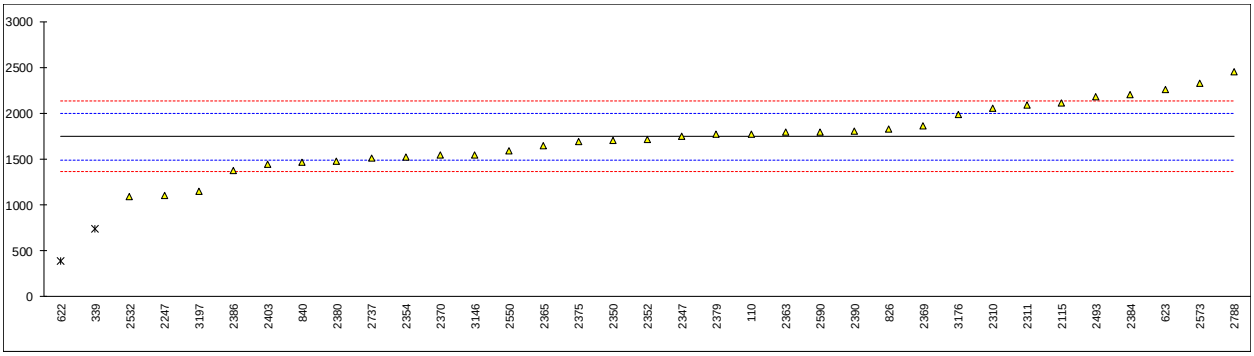
Each laboratory should evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

APPENDIX 1

Determination of PFOA on sample #17610; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	1773.96		0.22	
339	In house	738	R(0.01)	-7.85	
622	In house	388.35	ex, C	-10.57	See paragraph 4.1; first reported: 38816.88
623	CEN-TS15968	2253.29		3.95	
826	CEN-TS15968	1829.63		0.65	
840	CEN-TS15968	1470		-2.15	
2115	In house	2112.81	C	2.86	first reported: 8809.82
2247	CEN15968-mod	1106.44		-4.98	
2310	CEN-TS15968	2050		2.37	
2311	CEN-TS15968	2089.1		2.67	
2347	In house	1750		0.03	
2350	In house	1700.95		-0.35	
2352	EPA3540C/8321B	1713.2		-0.25	
2354	CEN-TS15968	1520.56		-1.75	
2363	INH-1135-T	1792		0.36	
2365	CEN-TS15968	1645.0		-0.78	
2369	CEN-TS15968	1858		0.87	
2370	CEN-TS15968	1540		-1.60	
2375	CEN-TS15968	1690.1		-0.43	
2379	CEN-TS15968	1770.91		0.20	
2380	CEN-TS15968	1479.93		-2.07	
2384	CEN-TS15968	2205.59		3.58	
2386	CEN-TS15968	1372.575412		-2.91	
2390	CEN-TS15968	1806.3		0.47	
2403	EPA3550C/8321B	1442.4		-2.36	
2493	In house	2179		3.37	
2532	CEN-TS15968	1090.6		-5.10	
2550	CEN-TS15968	1587.35		-1.23	
2573	CEN-TS15968	2327.0		4.53	
2590	CEN-TS15968	1797.72		0.40	
2737	In house	1514.209		-1.80	
2788	CEN-TS15968	2456.00		5.53	
3146	CEN-TS15968	1548		-1.54	
3163		-----		-----	
3176	CEN-TS15968	1988.0		1.89	
3197	CEN-TS15968	1150		-4.64	
3210		-----		-----	
3213		-----		-----	

normality	OK
n	33
outliers	1+1ex
mean (n)	1745.78
st.dev. (n)	341.437
R(calc.)	956.02
R(Horwitz 2 comp)	359.60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2000
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1000
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0
622
339
2532
2247
3197
2386
2403
840
2380
2737
2354
2370
3146
2550
2365
2375
2350
2352
2347
2379
110
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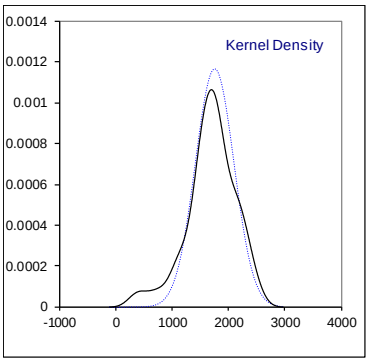
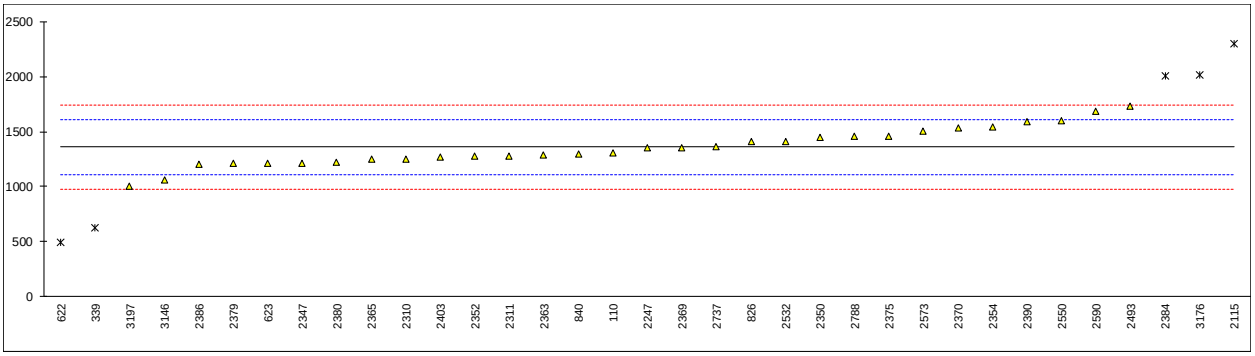
2390
826
2369
3176
2310
2311
2115
2493
2384
623
2573
2788


Kernel Density
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
-1000
0
1000
2000
3000
4000

Determination of PFOS on sample #17610; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	1304.26		-0.43	
339	In house	627	R(0.01)	-5.76	
622	In house	491.23	ex,C	-6.82	See paragraph 4.1; first reported: 49123.1
623	CEN-TS15968	1209.75		-1.17	
826	CEN-TS15968	1410.54		0.41	
840	CEN-TS15968	1300		-0.46	
2115	In house	2299.95	C,R(0.01)	7.40	first reported: 6049.95
2247	CEN15968-mod	1350.69		-0.06	
2310	CEN-TS15968	1250		-0.86	
2311	CEN-TS15968	1278.0		-0.63	
2347	In house	1210		-1.17	
2350	In house	1443.88		0.67	
2352	EPA3540C/8321B	1274.1		-0.67	
2354	CEN-TS15968	1544.70		1.46	
2363	INH-1135-T	1291		-0.53	
2365	CEN-TS15968	1248.9		-0.86	
2369	CEN-TS15968	1354		-0.04	
2370	CEN-TS15968	1530		1.35	
2375	CEN-TS15968	1455.6		0.76	
2379	CEN-TS15968	1208.31		-1.18	
2380	CEN-TS15968	1220.0		-1.09	
2384	CEN-TS15968	2007.34	R(0.01)	5.10	
2386	CEN-TS15968	1205.127978		-1.21	
2390	CEN-TS15968	1587.5		1.80	
2403	EPA3550C/8321B	1270.0		-0.70	
2493	In house	1733		2.94	
2532	CEN-TS15968	1412.1		0.42	
2550	CEN-TS15968	1598.17		1.88	
2573	CEN-TS15968	1508.5		1.18	
2590	CEN-TS15968	1681.45		2.54	
2737	In house	1360.06		0.01	
2788	CEN-TS15968	1453.73		0.75	
3146	CEN-TS15968	1060		-2.35	
3163		-----		-----	
3176	CEN-TS15968	2017.0	R(0.01)	5.18	
3197	CEN-TS15968	1008		-2.76	
3210		-----		-----	
3213		-----		-----	

normality	OK
n	30
outliers	4+1ex
mean (n)	1358.71
st.dev. (n)	171.202
R(calc.)	479.37
R(Horwitz 3 comp)	355.95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339
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2347
2380
2365
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2352
2311
2363
840
110
2247
2369
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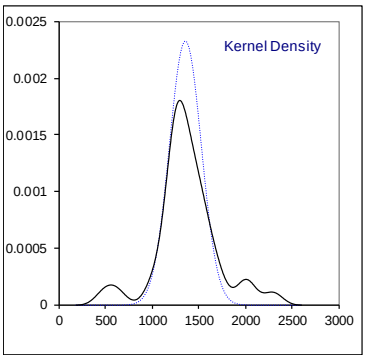
2390
2550
2590
2493
2384
3176
2115


Kernel Density
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0.002
0.0015
0.001
0.0005
0
0
500
1000
1500
2000
2500
3000

Determination of PFOA on sample #17611; results in mg/kg

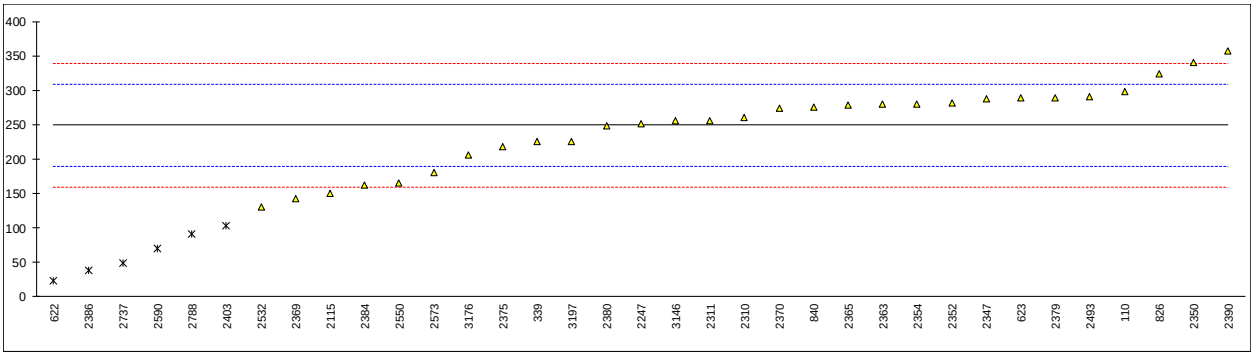
lab	method	value	mark	z(targ)	remarks
110	In house	ND		-----	
339	In house	0.102		-----	
622	In house	0.00		-----	
623	CEN-TS15968	n.d.		-----	
826	CEN-TS15968	<1.0		-----	
840	CEN-TS15968	nd		-----	
2115		n.d.		-----	
2247	CEN15968-mod	0.33		-----	
2310	CEN-TS15968	1.08		-----	
2311	CEN-TS15968	0.985		-----	
2347	In house	<10		-----	
2350	In house	<1.00		-----	
2352	EPA3540C/8321B	ND		-----	
2354	CEN-TS15968	ND		-----	
2363	EPA3540C/8321B	<10		-----	
2365	CEN-TS15968	ND		-----	
2369	CEN-TS15968	<10		-----	
2370	CEN-TS15968	n.d.		-----	
2375		<1		-----	
2379	CEN-TS15968	Not detected		-----	
2380		-----		-----	
2384	CEN-TS15968	<10		-----	
2386	CEN-TS15968	0.026		-----	
2390	CEN-TS15968	ND		-----	
2403	EPA3550C/8321B	<10		-----	
2493	In house	1.46		-----	
2532	CEN-TS15968	0.21		-----	
2550	CEN-TS15968	0.1562		-----	
2573	CEN-TS15968	0.505		-----	
2590	CEN-TS15968	0.081		-----	
2737	In house	0.033		-----	
2788	CEN-TS15968	0.13		-----	
3146	CEN-TS15968	<10		-----	
3163		-----		-----	
3176	In house	0.029		-----	
3197	CEN-TS15968	ND		-----	
3210		-----		-----	
3213		-----		-----	

normality	n.a.
N	23
outliers	0
mean (n)	<10
st.dev. (n)	n.a.
R(calc.)	n.a.
R(lit.)	n.a.

Determination of PFOS on sample #17611; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	297.75		1.62	
339	In house	225		-0.80	
622	In house	22.94	ex, C	-7.52	See paragraph 4.1; first reported: 114684.39
623	CEN-TS15968	289.23		1.33	
826	CEN-TS15968	324.19		2.50	
840	CEN-TS15968	275		0.86	
2115	In house	150.56		-3.28	
2247	CEN15968-mod	251.58		0.08	
2310	CEN-TS15968	260		0.36	
2311	CEN-TS15968	256.2		0.24	
2347	In house	287		1.26	
2350	In house	340.42		3.04	
2352	EPA3540C/8321B	281.8		1.09	
2354	CEN-TS15968	280.28		1.04	
2363	EPA3540C/8321B	279.6		1.01	
2365	CEN-TS15968	278.7		0.98	
2369	CEN-TS15968	142		-3.56	
2370	CEN-TS15968	274		0.83	
2375	CEN-TS15968	218.75		-1.01	
2379	CEN-TS15968	289.42		1.34	
2380	CEN-TS15968	248.31		-0.03	
2384	CEN-TS15968	162.5		-2.88	
2386	CEN-TS15968	37.9005683	R(0.01)	-7.02	
2390	CEN-TS15968	357.7		3.61	
2403	EPA3550C/8321B	103.3	R(0.05)	-4.85	
2493	In house	291		1.39	
2532	CEN-TS15968	130.2		-3.95	
2550	CEN-TS15968	164.53		-2.81	
2573	CEN-TS15968	181.0		-2.26	
2590	CEN-TS15968	70.62	R(0.01)	-5.93	
2737	In house	49.24	R(0.01)	-6.64	
2788	CEN-TS15968	91.6	C,R(0.05)	-5.24	first reported: 9.16
3146	CEN-TS15968	256		0.23	
3163		-----		-----	
3176	In house	205.40		-1.45	
3197	CEN-TS15968	225.8		-0.77	
3210		-----		-----	
3213		-----		-----	

normality	OK
n	29
outliers	5+1ex
mean (n)	249.10
st.dev. (n)	59.309
R(calc.)	166.06
R(Horwitz 3 comp)	84.24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200
150
100
50
0
622
2386
2737
2590
2788
2403
2532
2369
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2550
2573
3176
2375
339
3197
2380
2247
3146
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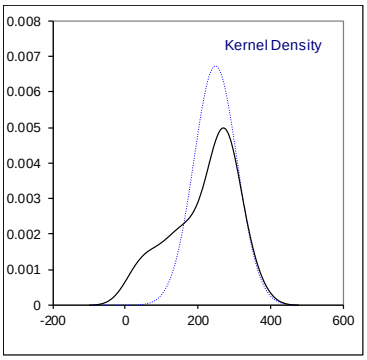
2347
623
2379
2493
110
826
2350
2390


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

APPENDIX 2 Analytical details

lab	Accredited acc. ISO /IEC17025 for this test?	Sample grinded or cut used as received	final estimated particle size	Used to release/extract the analyte(s)	Solvent (mixture) to release the analyte(s)	Extraction time (minutes)	Extraction temperature (°C)
110	Yes	Used as received	3mm x 3mm	Soxhlet	MeOH/DCM 1:1	360 minutes	Boiling
339	No	Cut	2 x 2 mm	Ultrasonic	Toluene / DCM 1:1	120 minutes	60°C
622	No	Cut	---	Ultrasonic	Methanol	10 minutes	25°C (room T)
623	No	Cut	2 mm x 2 mm	Ultrasonic	Methanol	120 minutes	60°C
826	No	Grinded	---	Ultrasonic	Methanol	120 minutes	60°C
840	Yes	Grinded	---	Ultrasonic	Methanol	120 minutes	60°C
2115	No	Used as received	---	Ultrasonic	MeOH/DCM 1:1	120 minutes	50°C
2247	Yes	Grinded	finely crushed (<1mm)	Ultrasonic	Methanol	120 minutes	70°C
2310	Yes	Cut	>1mm	Soxhlet	MeOH/DCM 1:1	360 minutes	70±2°C
2311	Yes	Cut	<1mm	Soxhlet	MeOH/DCM	360 minutes	80°C
2347	Yes	Cut	2mm*2mm*2mm	Ultrasonic	Methanol	60 minutes	70°C
2350	Yes	Cut	3 mm X 3 mm	Soxhlet	Methanol	360 minutes	
2352	Yes	Cut	2mm*2mm*2mm	Soxhlet	MeOH/DCM 1:1	360 minutes	105°C
2354	Yes	Cut	3mm X 4 mm (0.5g)	Soxhlet	MeOH/DCM	3600 minutes	100°C
2363	Yes	Cut	1mm*1mm	Ultrasonic (#17610), soxhlet (#17611)	MeOH (#17610), MeOH/DCM (#17611)	120 minutes (#17610), 480 minutes (#17611)	60°C (#17610)
2365	Yes	Cut	1mm*1mm	Soxhlet	MeOH/DCM 1:1	360 minutes	
2369	---	Used as received	5mmx5mm	Ultrasonic	Methanol	60 minutes	70°C
2370	Yes	Cut	=<1 mm	Soxhlet	MeOH/DCM	105 minutes	105°C
2375	No	Cut	2 mm x2 mm	Soxhlet	MeOH/DCM 1:1	90 minutes	105°C
2379	No	Cut	2 x 2 mm	Soxhlet	MeOH/DCM 1:1	360 minutes	
2380	Yes	Used as received	As Received	Soxhlet	MeOH/DCM	360 minutes	100°C
2384	Yes	Cut	---	Soxhlet	MeOH/DCM	360 minutes	
2386	Yes	Used as received	ca. 4x4 mm	Ultrasonic	Methanol	120 minutes	60°C
2390	Yes	Used as received	Approx 4mm	Soxhlet	MeOH/DCM 1:1	360 minutes	Not applicable
2403	Yes	Cut	<=0.5mm*0.5mm	Ultrasonic	Methanol	120 minutes	60°C
2493	Yes	Used as received	---	Ultrasonic	Tetrahydrofurane	60 minutes	40°C
2532	Yes	Cut	<1mm	Ultrasonic	MeOH:Water 1:1	120 minutes	60°C
2550	No	Cut	0.1-0.5mm	Ultrasonic	Methanol	120 minutes	40°C-60°C
2573	Yes	Cut	1mmx1mm	Ultrasonic	Methanol	120 minutes	60°C
2590	Yes	Cut	2x2 mm	Ultrasonic	Methanol	120 minutes	60°C
2737	Yes	Cut	3mm ~3mm	Ultrasonic	Methanol	120 minutes	60±2°C
2788	No	Cut	2mm x 2mm	Ultrasonic	Methanol	120 minutes	60°C
3146	Yes	Grinded	unknown (grinded)	Ultrasonic	Methanol	120 minutes	60°C
3163	---	---	---	---	---	---	---
3176	Yes	Cut	Approx..3mm	Ultrasonic	MeOH/DCM	120 minutes	60°C
3197	Yes	Cut	2 x 2 mm	Ultrasonic	Methanol	120 minutes	60°C
3210	---	---	---	---	---	---	---
3213	---	---	---	---	---	---	---

APPENDIX 3

Number of participating laboratories per country:

1 lab in BANGLADESH
2 labs in FRANCE
2 labs in GERMANY
1 lab in HONG KONG
1 lab in HUNGARY
4 labs in INDIA
2 labs in INDONESIA
2 labs in ITALY
3 labs in KOREA
1 lab in MALAYSIA
9 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in TAIWAN R.O.C.
1 lab in THAILAND
1 lab in THE NETHERLANDS
3 labs in TURKEY
2 labs in U.S.A.
1 lab in VIETNAM

APPENDIX 4

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
ex = test result excluded from statistical evaluation
n.a. = not applicable
n.e. = not evaluated
n.d. = not detected

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