Results of Proficiency Test
PFOA/PFOS
September 2016

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Report: iis16P09

October 2016

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1 INTRODUCTION

Perfluorooctanoic acid (PFOA) is one important representative of the substance group of per- and polyfluorinated substances (PFASs). The hazard profile of PFOA is well known: PFOA is a persistent, bioaccumulative, and toxic (PBT-) substance, which may cause severe and irreversible adverse effects on the environment and human health. PFOA has a harmonised classification in Annex VI of European Regulation (EC) No. 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP) as Carc. 2, Repr. 1B and STOT RE 1 (liver). Due to its PBT and CMR properties, PFOA and its ammonium salt (APFO) has been identified as substances of very high concern (SVHC) under REACH by unanimous agreement between EU Member States in July 2013.
Besides PFOA also other substances in the PFASs group 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 are also listed as substances of very high concern on the REACH candidate list because of their very persistent and very bioaccumulative properties. Perfluorooctane sulfonic acid (PFOS) is listed as persistent organic pollutant (POP) in Annex B of the Stockholm Convention.
The former restriction of PFOS under REACH and the current entry in Commission Regulation (EU) No.757/2010 (implementing Annex B of the Stockholm Convention) do not only cover PFOS itself, but also PFOS-related substances, which are outlined by the chemical formula: C8F17SO2X (X=OH, metal salt (O-M+), halide, amide, and other derivates including polymers). The reason for this is that these PFOS-related substances can be degraded to PFOS in the environment. (see lit.15)

In order 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 PFASs 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.”
Also the migration from food packaging has been subject of investigations.
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 2016, 59 laboratories from 20 different countries have 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 #16610 and #16611 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 April 2014 (iis-protocol, version 3.3). 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, #16610 artificially fortified to be positive on PFOS and #16611 artificially fortified with PFOA and PFOS, were selected. The materials were divided over 70 plastic bags, approx. 3 grams for each sample.
The homogeneity of the subsamples was checked by determination of PFOA/PFOS content on a number of stratified randomly selected subsamples. For sample #16610, the test results for PFOS varied between 1287 and 1383 mg/kg. For sample #16611, the test results for PFOA varied between 1008 and 1094 mg/kg and for PFOS between 153 and 166 mg/kg.
From the results of the homogeneity test, the relative between sample standard deviations RSD_r were calculated and compared with 0.3 times the relative proficiency target standard deviations RSD_R in agreement with the procedure of ISO 13528, Annex B2 in table 1 below.

	PFOS in #16610	PFOA in #16611	PFOS in #16611
RSD_r (observed)	3%	3%	3%
reference test method	Horwitz	Horwitz	Horwitz
0.3 x RSD_R (ref. test method)	2%	2%	2%
For comparison:			
0.3 x RSD_R (previous PTs)	19-25%	15-25%	19-25%

Table 1: relative repeatability standard deviations of PFOA/PFOS contents of the subsamples #16610 and #16611

The calculated variation coefficients RSDr for both samples are close to 0.3 times the strict estimated reference reproducibilities using the Horwitz equation, but they are at the same time far below to 0.3 times the corresponding estimated reproducibilities from previous proficiency tests (see table 3). Therefore, homogeneity of all subsamples was assumed.

To each of the participating laboratories one set of samples; 1 times sample #16610 and 1 times sample #16611 was sent on August 10, 2016.

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 results a detailed report form, on which the units were prescribed as well as the reference test methods and a letter of instructions were prepared and made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/.
The laboratories were also requested to confirm the sample receipt on the same data entry portal together with some details of the test methods used.

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 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 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 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 April 2014 (iis-protocol, version 3.3).
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. Not all data sets proved to have a normal distribution, in which cases the statistical evaluation of the test results should be used with due care.

According to ISO 5725 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. 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 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. 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 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, e.g. ISO reproducibilities, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation of this interlaboratory study. The target standard deviation was calculated from the literature reproducibility by division with 2.8.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate whether the reported test result is fit-for-use.
The z-scores were calculated according to:

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

The $z_{(target)}$ scores are listed in the test result tables in appendix 1.
Absolute values for z<2 are very common and absolute values for z>3 are very rare.

The usual interpretation of z-scores is as follows:

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

4 EVALUATION

In this interlaboratory study, no problems were encountered with the dispatch of the samples. Two participants reported test results after the final reporting date and eleven other participants did not report any test result at all. Finally, the 48 reporting laboratories reported 162 numerical results. Observed were 10 outlying test results, which is 5.8%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

For all data sets a normal distribution was found.

For the determination of PFOA/PFOS, the CEN-TS 15968 method is considered to be the official EC test method by the majority of the participating laboratories. However the scope of this method is more 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.

4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this section the results are discussed per sample and per test.

#16610: PFOA: All of the 45 reporting participants agreed on the absence of PFOA on a concentration level lower than 10 mg/kg. The majority reported n.d. or lower than 1 (or lower) mg/kg.
The material had not been spiked with PFOA and it was decided not to calculate a z-score for this determination.

#16610:PFOS: Severe analytical problems were observed in determining the PFOS concentration at a level of 972 mg/kg. The reported PFOS concentration varies over a large range from 149.0 to 1188.1 mg/kg. Seven statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility calculated using the Horwitz equation.

#16611:PFOA Severe analytical problems were observed in determining the PFOA concentration at a level of 833 mg/kg. The reported PFOA concentration varies over a large range from 394.8 to 1515.7 mg/kg. Two statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the estimated reproducibility calculated using the Horwitz equation.

#16611:PFOS Severe analytical problems were observed in determining the PFOS concentration at a level of 123.4 mg/kg. The reported PFOS concentration varies over a range from 39.4 to 172.8 mg/kg. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated reproducibility calculated using the Horwitz equation.

4.2 PERFORMANCE EVALUATION OF THE GROUP OF LABORATORIES

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

	unit	n	Average	2.8 * sd	R(Horwitz)
PFOA in #16610	mg/kg	45	<10	n.a.	n.a.
PFOS in #16610	mg/kg	41	972	302	155
PFOA in #16611	mg/kg	45	833	411	136
PFOS in #16611	mg/kg	47	123	65	27

Table 2: performance overview for all received test results on samples #16610 and #16611

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

4.3 EVALUATION OF THE TEST METHODS USED

Almost the half of the participants (44%) reported to have used an 'in house' test method and 48% of the participants reported to have used the CEN/TS 15968 method for the determination of PFOA/PFOS. Another four participants reported to have used EPA3540C. The reported details of the methods that were used by the participants are listed in appendix 2. The effect of pre-treatment of the granulate on the PFOS determination is only visible for sample #16610. Participants that did mention to have used the granulate 'as received' reported lower values for PFOS in sample #16610 in comparison with the participants that reported to have grinded or milled the granulate before use.

4.4 COMPARISON OF PROFICIENCY TEST OF SEPTEMBER 2016 AGAINST PREVIOUS PTS

The observed variation expressed as relative standard deviation RSD of the test results in the 2016 PT did improve in comparison with the observations in previous PTs, see below table.

RSD%	*2016*	*2015*	*2014*	*2013*	*2011 - 2012*	*Target Horwitz 100-1000 mg/kg*
PFOA sample 1	n.d.	n.d.	n.d.	n.d.	15-30%	6 - 8%
PFOA sample 2	18%[a]	n.d.	144%	29%	19%	6 - 8%
PFOS sample 1	11%[a]	25[s] - 58%[a]	62[s] - 128%[a]	162%	141%	6 - 8%
PFOS sample 2	19%[a]	24[s] - 61%[a]	27[s] - 53%[a]	n.d.	Not in PT	6 - 8%

Table 3: development of uncertainties, reported as RSD, over **all (a**) or over **subset (s)** of results against previous PTs

For PFOA/PFOS the target value for the precision of the PFOA and PFOS content determination in polymers was based on the Horwitz equation. This target value of 6 - 8% appears to be very optimistic. Based on the performance in this proficiency test a value lower than 18 - 19% for the variation coefficient is more feasible when participants use an effective method for sample pre-treatment and extraction (see also paragraph 5 for more discussion)

5 DISCUSSION

Overall, it is clear that the group of participants performed much better in the 2016 proficiency test than in the previous iis proficiency tests on PFOA/PFOS. All observed reproducibilities in the 2016 PT were smaller than before.
However, the calculated reproducibilities were still not in agreement compared against the (strict) reproducibilities estimated from the Horwitz equation.

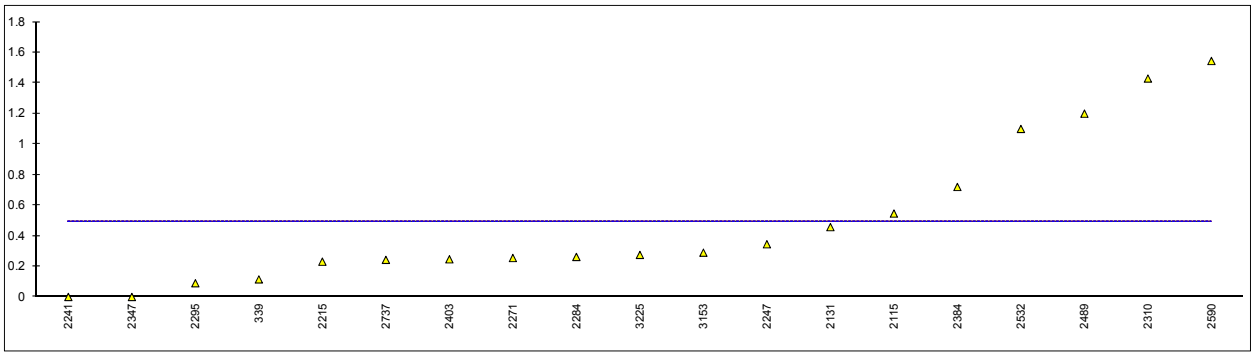
The conclusion is that the majority of the participants may be able to determine PFOA and PFOS in the polymer matrix, but still a large variation is found between participant's test results. This variation obviously is dependent on the chosen sample pre-treatment and extraction procedure. Not surprisingly, 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 pathways could be cutting, milling or grinding the polymer prior the extraction. However, it is important to realize what kind of determination is requested by the applicant. In case of a migration request the cutting or grinding may not be appropriate and the material should probably best be treated as received. In the case of a total content determination request the polymer matrix should be reduced to small particles, in order to increase the contact surface and thus to facilitate the release of PFOA and PFOS from the matrix.

Each laboratory has to 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 #16610; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	ND		-----	
339	In house	0.115		-----	
623	In house	n.d.		-----	
840	CEN-TS15968	ND		-----	
2115	In house	0.546		-----	
2131	In house	0.45725		-----	
2132	In house	<1		-----	
2212		-----		-----	
2215	In house	0.231		-----	
2216		-----		-----	
2241	In house	0		-----	
2247	In house	0.345		-----	
2255	CEN-TS15968	nd		-----	
2271	CEN-TS15968	0.255		-----	
2284	In house	0.262		-----	
2295	CEN-TS15968	0.09		-----	
2310	CEN-TS15968	1.43		-----	
2320	CEN-TS15968	N.D		-----	
2330		-----		-----	
2347	In house	0		-----	
2350	In house	<1.00		-----	
2352	EPA3540C/8321B	ND		-----	
2354	In house	<10		-----	
2365	EPA3540C/8321B	<10		-----	
2370	CEN-TS15968	n.d.		-----	
2375	CEN-TS15968	< 1		-----	
2379	CEN-TS15968	ND		-----	
2380	CEN-TS15968	ND		-----	
2384	CEN-TS15968	0.72		-----	
2386	In house	<5		-----	
2390	CEN-TS15968	ND		-----	
2403	EPA3540C/8321B	0.2467		-----	
2415	CEN-TS15968	ND		-----	
2425	In house	ND		-----	
2482		-----		-----	
2489	CEN-TS15968	1.2		-----	
2510		-----		-----	
2532	CEN-TS15968	1.1		-----	
2549	In house	ND		-----	
2560	In house	<1		-----	
2590	CEN-TS15968	1.545		-----	
2668	CEN-TS15968	ND		-----	
2710		-----		-----	
2713		-----		-----	
2737	CEN-TS15968	0.2427		-----	
2749		-----		-----	
3100	In house	<0.5		-----	
3118		-----		-----	
3146		-----		-----	
3153	CEN-TS15968	0.29		-----	
3172	CEN-TS15968	n.d.		-----	
3176		-----		-----	
3182	CEN-TS15968	<1		-----	
3197	CEN-TS15968	ND		-----	
3200		-----		-----	
3210		-----		-----	
3218	CEN-TS15968	<0.5	C	-----	First reported 470.4
3225	In house	0.27540		-----	
3237		-----		-----	
	normality	n.a.			
	n	45			
	outliers	n.a.			
	mean (n)	<10			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(lit)	n.a.			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1.6
1.4
1.2
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2241
2347
2295
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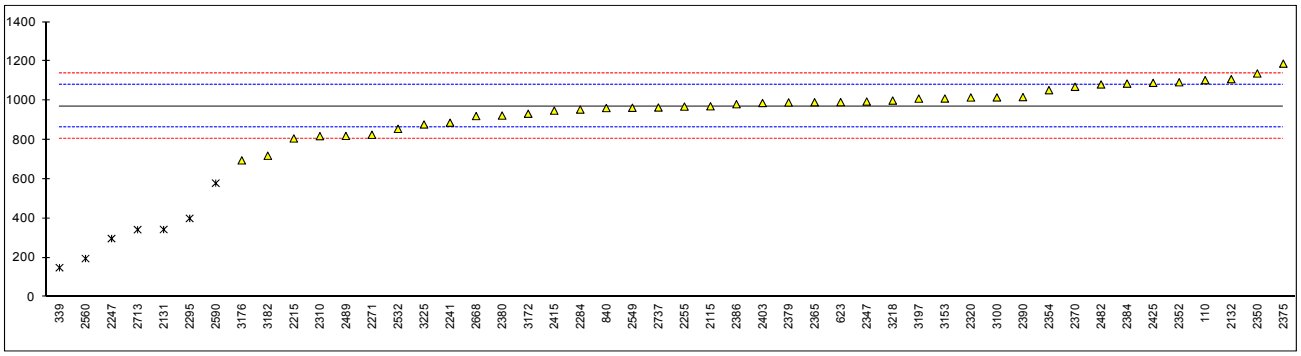
2215
2737
2403
2271
2284
3225
3153
2247
2131
2115
2384
2532
2489
2310
2590

Determination of PFOS on sample #16610; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	1104		2.40	
339	In house	149	R(0.01)	-14.90	
623	In house	992.09		0.37	
840	CEN-TS15968	962		-0.18	
2115	In house	970.73		-0.02	
2131	In house	343.25	R(0.01)	-11.38	
2132	In house	1109.00	C	2.49	First reported 1489.43
2212		-----		-----	
2215	In house	807.1		-2.98	
2216		-----		-----	
2241	In house	887.3		-1.53	
2247	In house	297.12	R(0.01)	-12.22	
2255	CEN-TS15968	969.3		-0.04	
2271	CEN-TS15968	826		-2.64	
2284	In house	954.27		-0.32	
2295	CEN-TS15968	400.0	C,R(0.01)	-10.36	First reported 249.6
2310	CEN-TS15968	819		-2.77	
2320	CEN-TS15968	1015.72		0.80	
2330		-----		-----	
2347	In house	995		0.42	
2350	In house	1138		3.01	
2352	EPA3540C/8321B	1093.1		2.20	
2354	In house	1053		1.47	
2365	EPA3540C/8321B	991.5		0.36	
2370	CEN-TS15968	1070		1.78	
2375	CEN-TS15968	1188.1		3.92	
2379	CEN-TS15968	990.44		0.34	
2380	CEN-TS15968	923.7		-0.87	
2384	CEN-TS15968	1086.40		2.08	
2386	In house	981.3		0.17	
2390	CEN-TS15968	1017.87		0.84	
2403	EPA3540C/8321B	987.5		0.29	
2415	CEN-TS15968	948.7		-0.42	
2425	In house	1090.3		2.15	
2482	EPA3540C/8321B	1082		2.00	
2489	CEN-TS15968	820		-2.75	
2510		-----		-----	
2532	CEN-TS15968	856		-2.10	
2549	In house	963.3		-0.15	
2560	In house	195.6485	C,R(0.01)	-14.06	First reported 295.6485
2590	CEN-TS15968	579.357	C,R(0.05)	-7.11	First reported 443.256
2668	CEN-TS15968	921		-0.92	
2710		-----		-----	
2713	In house	342.4189	C,R(0.01)	-11.40	First reported 228.4531
2737	CEN-TS15968	964.7		-0.13	
2749		-----		-----	
3100	In house	1016.0	C	0.80	First reported 546.9
3118		-----		-----	
3146		-----		-----	
3153	CEN-TS15968	1010.5		0.70	
3172	CEN-TS15968	933		-0.70	
3176	In house	695.40		-5.01	
3182	CEN-TS15968	719.1		-4.58	
3197	CEN-TS15968	1010		0.69	
3200		-----		-----	
3210		-----		-----	
3218	CEN-TS15968	1000.0	C	0.51	First reported <0.5
3225	In house	878.44		-1.69	
3237		-----		-----	

normality	OK
n	41
outliers	7
mean (n)	971.73
st.dev. (n)	107.764
R(calc.)	301.74
R(Horwitz)	154.58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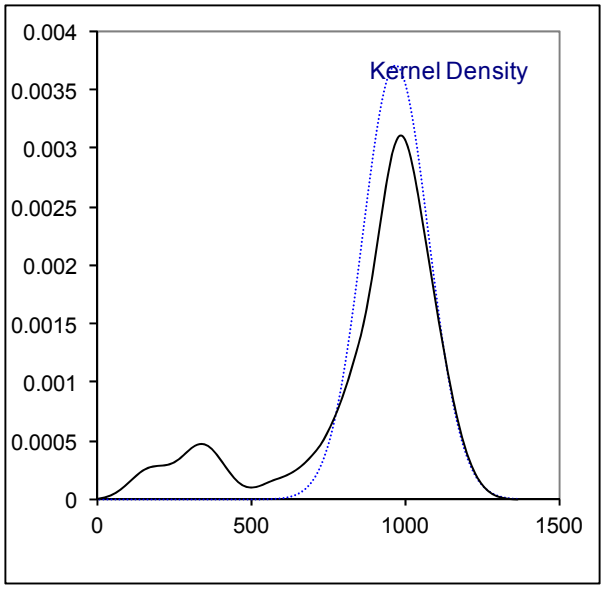
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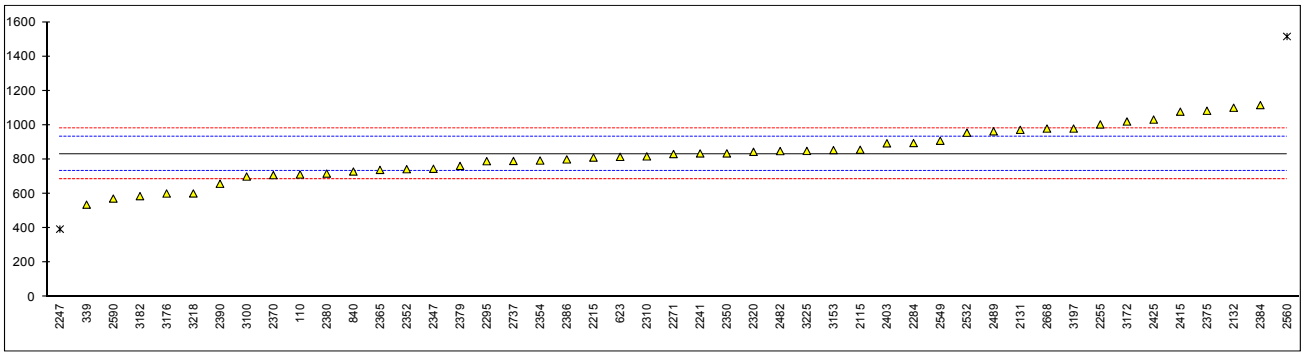
0.0025
0.002
0.0015
0.001
0.0005
0
0
500
1000
1500

Determination of PFOA on sample #16611; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	712.7		-2.49	
339	In house	537.2		-6.11	
623	In house	815.47		-0.36	
840	CEN-TS15968	730		-2.13	
2115	In house	856.76		0.49	
2131	In house	972.5		2.88	
2132	In house	1101	C	5.53	First reported 1537.17
2212		-----		-----	
2215	In house	811.2		-0.45	
2216		-----		-----	
2241	In house	835.1		0.04	
2247	In house	394.840	R(0.05)	-9.05	
2255	CEN-TS15968	1004.1		3.53	
2271	CEN-TS15968	831.8		-0.03	
2284	In house	895.75		1.29	
2295	CEN-TS15968	790	C	-0.89	First reported 533
2310	CEN-TS15968	818		-0.31	
2320	CEN-TS15968	844.77		0.24	
2330		-----		-----	
2347	In house	746		-1.80	
2350	In house	835.5		0.05	
2352	EPA3540C/8321B	743.4		-1.85	
2354	In house	794		-0.81	
2365	EPA3540C/8321B	739.5		-1.93	
2370	CEN-TS15968	709		-2.56	
2375	CEN-TS15968	1083.5		5.17	
2379	CEN-TS15968	762.54		-1.46	
2380	CEN-TS15968	718.1		-2.37	
2384	CEN-TS15968	1116.44		5.85	
2386	In house	800.5		-0.67	
2390	CEN-TS15968	658.98		-3.59	
2403	EPA3540C/8321B	894.21		1.26	
2415	CEN-TS15968	1078.4		5.06	
2425	In house	1032.2		4.11	
2482	EPA3540C/8321B	849		0.33	
2489	In house	964		2.70	
2510		-----		-----	
2532	CEN-TS15968	956		2.54	
2549	In house	909		1.57	
2560	In house	1515.707	R(0.01)	14.09	
2590	CEN-TS15968	572.499		-5.38	
2668	CEN-TS15968	980		3.03	
2710		-----		-----	
2713		-----		-----	
2737	CEN-TS15968	791.5		-0.86	
2749		-----		-----	
3100	In house	700.9		-2.73	
3118		-----		-----	
3146		-----		-----	
3153	CEN-TS15968	854.9		0.45	
3172	CEN-TS15968	1021		3.88	
3176	In house	602	C	-4.77	First reported 352.2
3182	CEN-TS15968	586.7		-5.09	
3197	CEN-TS15968	980		3.03	
3200		-----		-----	
3210		-----		-----	
3218	CEN-TS15968	602.4	C	-4.76	First reported 121.7
3225	In house	849.802		0.35	
3237		-----		-----	

normality	OK
n	45
outliers	2
mean (n)	833.07
st.dev. (n)	146.939
R(calc.)	411.43
R(Horwitz)	135.63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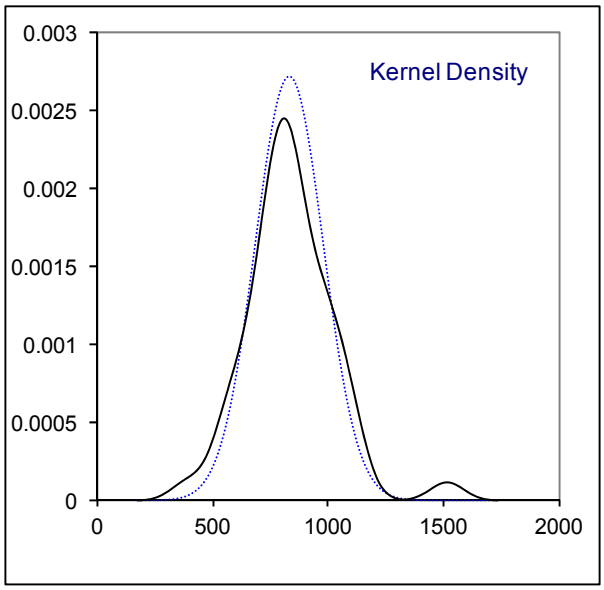
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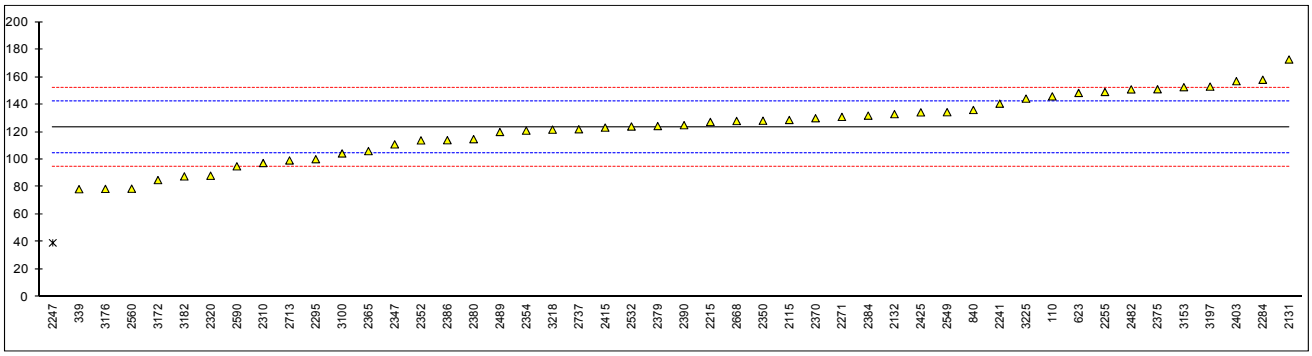
0.001
0.0005
0
0
500
1000
1500
2000

Determination of PFOS on sample #16611; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	In house	145.9		2.35	
339	In house	78.4		-4.71	
623	In house	148.41		2.61	
840	CEN-TS15968	136		1.32	
2115	In house	128.72		0.55	
2131	In house	172.75		5.16	
2132	In house	133	C	1.00	First reported 177.93
2212		-----		-----	
2215	In house	127.3		0.41	
2216		-----		-----	
2241	In house	140.6		1.80	
2247	In house	39.364	R(0.05)	-8.79	
2255	CEN-TS15968	149.1		2.69	
2271	CEN-TS15968	131		0.79	
2284	In house	157.99		3.61	
2295	CEN-TS15968	100.2		-2.43	
2310	CEN-TS15968	97.4		-2.72	
2320	CEN-TS15968	88.17		-3.68	
2330		-----		-----	
2347	In house	111		-1.30	
2350	In house	128.2		0.50	
2352	EPA3540C/8321B	113.9		-0.99	
2354	In house	121		-0.25	
2365	EPA3540C/8321B	106.1		-1.81	
2370	CEN-TS15968	130		0.69	
2375	CEN-TS15968	151.1		2.89	
2379	CEN-TS15968	124.31		0.09	
2380	CEN-TS15968	114.8		-0.90	
2384	CEN-TS15968	131.90		0.89	
2386	In house	114.04	C	-0.98	First reported 1140.4
2390	CEN-TS15968	124.99		0.16	
2403	EPA3540C/8321B	156.97		3.51	
2415	CEN-TS15968	123.2		-0.02	
2425	In house	134.3		1.14	
2482	EPA3540C/8321B	151		2.88	
2489	In house	120		-0.36	
2510		-----		-----	
2532	CEN-TS15968	124		0.06	
2549	In house	134.4		1.15	
2560	In house	78.72773		-4.67	
2590	CEN-TS15968	95.021		-2.97	
2668	CEN-TS15968	128		0.48	
2710		-----		-----	
2713	In house	99.3038		-2.52	
2737	CEN-TS15968	122.0		-0.15	
2749		-----		-----	
3100	In house	104.4		-1.99	
3118		-----		-----	
3146		-----		-----	
3153	CEN-TS15968	152.6		3.05	
3172	CEN-TS15968	85		-4.02	
3176	In house	78.60		-4.69	
3182	CEN-TS15968	87.7		-3.73	
3197	CEN-TS15968	153		3.09	
3200		-----		-----	
3210		-----		-----	
3218	CEN-TS15968	121.7	C	-0.18	First reported 602.4
3225	In house	144.269		2.18	
3237		-----		-----	

normality	OK
n	47
outliers	1
mean (n)	123.41
st.dev. (n)	23.314
R(calc.)	65.28
R(Horwitz)	26.78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60
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20
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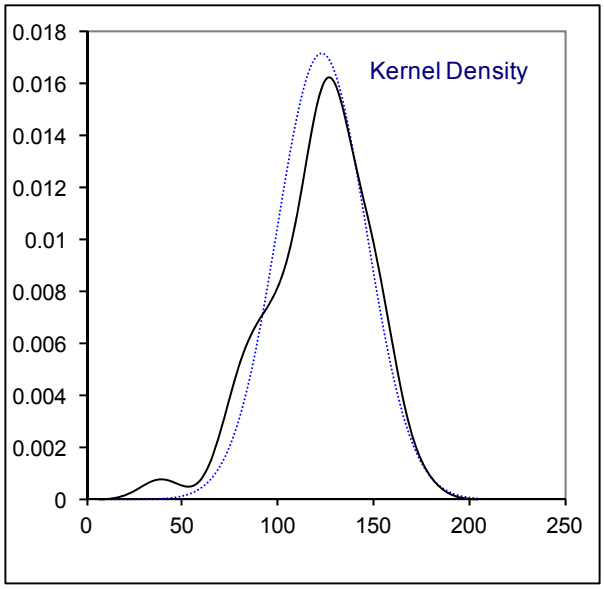
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0.012
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0.004
0.002
0
0
50
100
150
200
250

APPENDIX 2 Analytical details

lab	Was sample grinded, cut or used as received	Final estimated particle size	Type of technique used	Solvent mixture used	Extraction time and temperature
110	Cut	3 x 3 mm	Soxhlet	Methanol: DCM 1:1	6 hrs Reflux
339	Used as received	0.3 x 0.3 mm	Ultrasonic	Methanol	60 min at ambient temperature
623	Cut	2 x 2 mm	Soxhlet	Methanol: DCM	6 hrs
840	Cut	2 x 2 mm	Soxhlet	Methanol: DCM	60 min at 105°C
2115	Cut	2 mm	Ultrasonic	Methanol: DCM 1:1	2 hrs at 50°C
2131	Used as received	---	ASE	Methanol	15 80
2132	Grinded	Powder	Ultrasonic	Methanol	2 hrs at 60°C
2212	---		---		
2215	Cut	0.2mm	Ultrasonic	Methanol	2 hrs
2216	---		---		
2241	Cut	1 x 1 mm	Ultrasonic	Methanol	60 min for 2hours
2247	Used as received	>1mm	Ultrasonic	Methanol	60
2255	Cut	as much possible	Ultrasonic	Methanol	120 min at 60°C
2271	Cut	2 x 2 mm	Ultrasonic	Methanol	120 min at 60°C
2284	Cut	1 x 1 mm	Soxhlet	Methanol: DCM 1:1	6hours
2295	Cut	about 2mm	Ultrasonic	Methanol	120 min at 60°C
2310	Cut	>1mm	Soxhlet	Methanol: DCM 1:1	6 hrs at 70±2˚C
2320	Cut	2 × 2 mm	Soxhlet	Methanol: DCM 1:1	6 hrs at boiling water bath
2330	---		---		
2347	Cut	2 x 2 mm	Ultrasonic	Methanol	60 min at 70°C
2350	Cut	3 x 3 mm	Soxhlet	Methanol	6 hrs
2352	Cut	<1mm	Soxhlet	Methanol: DCM 1:1	6 hrs at 105°C
2354	Cut	3 x 3 mm	Soxhlet	Methanol: DCM 1:1	0.5 hr
2365	Cut	<1mm	Soxhlet	Methanol: DCM 1:1	6 hrs
2370	Cut	=<1 mm	Soxhlet	Methanol: DCM	1hr45mins at 105°C
2375	Cut	2 x 2 mm	Soxhlet	Methanol: DCM 1:1	30 min at 105°C
2379	Cut	1 x 1 mm.	Soxhlet	Methanol: DCM 1:1	6 hr.
2380	Used as received	--	Soxhlet	Methanol: DCM 1:1	360 min at 85+/-3 °C
2384	Cut	<500um	Soxhlet	Methanol: DCM 1:1	6 hrs, reflux
2386	Grinded		Ultrasonic	Aceton/Acetonitril	60 min at 40°C
2390	Cut	2 mm approx	Soxhlet	Methanol: DCM 1:1	360 min.
2403	Cut	<=0.5mm	Soxhlet	Methanol: DCM	6h reflux
2415	Cut	5mm	Ultrasonic	Methanol	2 hrs at 60°C
2425	Cut	2 x 2 mm	Ultrasonic	Methanol: DCM 1:1	2 hrs at 70°C
2482	Cut	< 1 mm	Soxhlet	Methanol: DCM 1:1	6 hrs

lab	Was sample grinded, cut or uses as received	Final est. particle size	Type of technique used	Solvent mixture used	Extraction time and temperature
2489	Cut	<2mm	Ultrasonic	Methanol	2 hrs at 60°C
2510	---		---		
2532	Cut	equivalent to powder	Ultrasonic	Methanol	2 hrs at 60°C
2549	Cut	2 x 2 mm	Ultrasonic	Methanol: DCM 1:1	2 hrs at 60°
2560	Used as received	3-4 mm	Ultrasonic	Methanol	60 min and room temperature
2590	Cut	around 2 mm	Ultrasonic	Methanol	2 hrs at 60 °C
2668	Cut	1 mm	Ultrasonic	Methanol	2 hrs
2710	---		---		
2713	Used as received	---	Ultrasonic	Methanol	120 min at 60 °C
2737	Used as received	---	Ultrasonic	Methanol	120 min at 60°C
2749	---		---		
3100	Grinded	<500 µm	Ultrasonic	Methanol	2 hrs at70°C
3118	---		---		
3146	---		---		
3153	Cut	2 x 2 mm	Ultrasonic	Methanol	120 min at 60°C
3172	Grinded	Dust	Ultrasonic	Methanol	1h at 60°C
3176	Cut	2 mm	Soxhlet	Methanol: DCM	6 hrs at 150°C
3182	Grinded	500 µm	Ultrasonic	Methanol	120 minutes at 60°C
3197	Cut	<0,5 mm	Ultrasonic	Methanol	120 minutes at 60°C
3200					
3210	---		---		
3218	Grinded	<1mm	Ultrasonic	Methanol	2 hours, 60 degrees centigrade
3225	Cut	2 x 3 mm	Ultrasonic	Methanol	120 minutes (2 hours) and 60°C
3237	---		---		

APPENDIX 3

Number of participating laboratories per country:

4 labs in BANGLADESH
1 lab in CAMBODIA, Kingdom of
2 labs in FRANCE
3 labs in GERMANY
5 labs in HONG KONG
6 labs in INDIA
2 labs in INDONESIA
1 lab in IRELAND
3 labs in ITALY
1 lab in KOREA
1 lab in MALAYSIA
12 labs in P.R. of CHINA
1 lab in PAKISTAN
1 lab in SRI LANKA
2 labs in SWITZERLAND
1 lab in TAIWAN R.O.C.
2 labs in THAILAND
6 labs in TURKEY
3 labs in U.S.A.
2 labs 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 outlier test
R(0.05) = straggler in Rosner outlier test
ex = test result excluded from calculations
n.a. = not applicable
n.e. = not evaluated
n.d. = not detected

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