Results of Proficiency Test PFOA/PFOS September 2014

SUMMARY OF CHANGES

This revised report replaces the original report iis14P07 of October 2014.

One of the participants reported by e-mail (13th November 2014) the presence of an error in the original report iis14P07. It appeared that the calculation of the z-scores for PFOS in sample #14155 was not correct.
The z-scores in the original report were not based on the selected data (the 13 test results after cryogenic milling) as intended and described in the report, but on all reported test results.
Therefore the following pages in this report have been revised:

- the z-scores in the table on page 16 (page 15 in the original report)

CONTENTS

Appendices:

1   INTRODUCTION

Worldwide, many consumer products are produced that contain Teflon parts. In the production of Teflon, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been used. PFOA/PFOS persist indefinitely in the environment. It is a toxicant and carcinogen in animals.

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 perfluorooctane sulfonate ($C_8F_{17}SO_2X$, where X may be OH, being PFOA) is restricted: "Semi-finished products or articles, or parts thereof, if the concentration of PFOS 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 in the 2012 PT program. This PT was continued each following year. In the interlaboratory study of September 2014, 57 laboratories from 20 different countries participated (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 internet site www.iisnl.com.

2   SET-UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, The Netherlands, was the organiser of this proficiency test. It was decided to send 2 different plastic samples (approximately 5 gram each), positive (artificially fortified) on PFOA or PFOS and labelled #14154 and #14155 respectively. Participants were also requested to report a number of details of the test method used.

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, see also www.RVA.nl). This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentially 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 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 can be downloaded from the iis website www.iisnl.com.

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 samples, #14154 artificially fortified to be positive on PFOS (theoretically 0.06%M/M) and #14155 artificially fortified with PFOS (theoretically 0.06%M/M), were selected. The materials were divided over plastic bags, approx. 5 grams for each sample. The homogeneity of the subsamples was checked by determination of PFOS and PFOA content on a number of stratified randomly selected subsamples. For sample #14154, the test results varied for PFOS between 0.0562 and 0.0587%M/M. For sample #1455, the test results varied for PFOS between 0.0569 and 0.0611%M/M.

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 the next table:

	PFOS in #14154	PFOS in #14155
RSD_r (observed)	1%	2%
reference method	Horwitz	Horwitz
0.3 x RSD_R (reference method)	2%	2%

Table 1: relative repeatability standard deviations of PFOS contents of the subsamples #14154 and #14155

The calculated variation coefficients RSDr are in full agreement with the estimated targets, calculated using the Horwitz equation, for both samples. Therefore, homogeneity of all subsamples was assumed.

To each of the participating laboratories one set of samples, (1* sample #14154 and 1* sample #14155) was sent on August 13, 2014.

2.5 ANALYSIS

The participants were requested to determine PFOA and PFOS 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 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 a letter of instructions were prepared and made available for download on the iis website. A form to confirm receipt of the samples was also added to the sample package.

The laboratories were requested to complete the report form with some details of the methods used.

3   RESULTS

During four weeks after sample despatch, the results of the individual laboratories were received. The original data are tabulated per sample in the appendix 1 of this report.
The laboratories are represented by the code numbers.
Directly after the deadline, a reminder fax was sent to those laboratories that did not report results at that moment.
Shortly after the deadline, the available results were screened for suspect data. A 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 results. Additional or corrected results are used for the data analysis and the original results are placed under 'Remarks' in the result tables in appendix 1.

3.1   STATISTICS

The statistical calculations were performed as described in the procedures in the report 'iis Interlaboratory Studies, Protocol for the Organisation, Statistics and Evaluation' of April 2014 (iis-protocol, version 3.3).

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 results should be used with due care.

In accordance to ISO 5725 (1986 and 1994) the original results per determination were submitted subsequently to Dixon, Grubbs and or Rosner General ESD outlier tests. Outliers are marked by D(0.01) for the Dixon test, by G(0.01) or DG(0.01) for the Grubbs test and by R(0.01) for the Rosner General ESD test. Stragglers are marked by D(0.05) for the Dixon test, by G(0.05) or DG(0.05) for the Grubbs test and by R(0.05) for the Rosner General ESD test (ref. 15). Both outliers and stragglers were not included in the calculations of averages and standard deviations.

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

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.

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 analysis results are plotted. The corresponding laboratory numbers are under 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 standard. 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 (see appendix 4; ref. 13 and 14). 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 spread of this interlaboratory study. The target standard deviation was calculated from the target reproducibility (preferably taken from a standardized test method) by division with 2.8.

The standard uncertainly (u_x) was calculated from the (target) standard deviation in accordance with ISO13528, paragraph 5.6:

$$u_x = 1.25 * (st.dev (n)) / \sqrt{n}$$

In ISO13528 is stated that if $u_x \geq 0.3 *$ standard deviation for proficiency testing, the uncertainly of the assigned value is not negligible and need to be included in the interpretation of the results of the proficiency test. Therefore in this PT report z'-scores were calculated in stead of the usual z-scores. The z'(target)-scores were calculated in accordance with ISO13528 paragraph 7.6:

$$z'(target) = (result - mean of PT) / \sqrt{((target standard deviation)^2 + (u_x)^2)}$$

The z'(target) scores are listed in the 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:

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

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.

4   EVALUATION

In this interlaboratory study, no problems were encountered with the dispatch of the samples. Forteen participants reported test results after the final reporting date and four other participants did not report any test results at all.
Finally, the 53 reporting laboratories reported 132 numerical results. Observed were 8 outlying results, which is 5.7%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

A not-normal distribution was found for the full data set of reported PFOS test results of sample #14154 and the PFOA test results of sample #14155. Therefore these statistical evaluations should be used with due care.

For the determination of PFOA/PFOS, the CEN/TS 15968 method is considered to be the official EC test method. Regretfully this method does not yet mention reproducibility requirements. Therefore, the target requirements in this study were estimated using the Horwitz equation. Furthermore, it was decided to use assigned consensus values based on a sub set of test results, determined after cryogenic milling of the samples, see also paragraphs 4.3 and 5.

4.1   PERFORMANCE EVALUATION OF THE GROUP OF LABORATORIES

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

	unit	n	Average	2.8 * sd	R'(Horwitz)
PFOA in #14154	%M/M	20	<0.001	n.a.	n.a.
PFOS in #14154	%M/M	46	0.00904	0.00324	(0.00066)
PFOA in #14155	%M/M	22	0.00004	0.00018	(0.00005)
PFOS in #14155	%M/M	51	0.03999	0.05915	0.01265

Table 2: performance overview for all received test results on samples #14154 and #14155

Without further statistical calculations, it can be concluded that there is not a good compliance of the group of participating laboratories with the target reproducibility.

4.2   EVALUATION PER SAMPLE

In this section the results are discussed per sample.

#14154: Severe analytical problems were observed at the theoretical concentration level of
0.06%M/M PFOS in the evaluated material. The majority of the reporting
laboratories did detect only very small quantities of PFOS (< 0.006%M/M) in sample
#14154. Fifty laboratories reported a numerical test result below 0.01%M/M. After
exclusion of 4 statistical outliers the average concentration PFOS is approx
0.0009%M/M. However, four participants reported results between 0.01%M/M and
0.04%M/M being in better agreement with the theoretical PFOS amount of
0.06%M/M. Due to the on average very low recovery it was decided not to calculate
any z-scores for this determination. See also paragraph 4.3.
All reporting participants, except one, agreed on the absence of PFOA on a
concentration level of <0.001%M/M.

#14155: Severe analytical problems were observed at the theoretical concentration level of
0.06%M/M PFOS in the evaluated material. The assigned consensus value, based
on a selected number of test results was 0.047%M/M, which is slightly higher than
the average value of all reported test results, see paragraph 4.3. The calculated
reproducibility, after rejection of two statistical outliers is not in agreement with the
estimated reproducibility limits calculated using the Horwitz equation. The average
recovery of PFOS is 78%.
All reporting participants, except one, agreed on the absence of PFOA on a
concentration level of <0.001%M/M.

4.3   EVALUATION OF THE TEST METHODS USED

The majority of the participants reported to have used an 'in house' test method and only 13
participants reported to have used the CEN/TS 15968 method. Another three participants
reported to have used DIN38407 or the EPA3540 or 3550 methods. The reported details of
the methods that were used by the participants are listed in appendix 2.
The majority of the participants used methanol or methanol/dichloromethane 1:1 to release
PFOA and PFOS from the plastic matrix. Four participants reported to have used THF or a
THF/2nd solvent mixture and two other participants used Acetonitrile or Acetone. The test
results of the three laboratories (2139, 2603 and 3210) that used THF were significantly
higher than the test results of the participants that did not use THF, see table 3.

	Solvent used	unit	n	average	st.dev
PFOS in #14154	All solvents except THF mixtures	%M/M	45	0.0008	0.0009
PFOS in #14154	THF/MeOH or THF/chlorobenzene	%M/M	3	0.0328	0.0143
PFOS in #14155	All solvents except THF mixtures	%M/M	48	0.0381	0.0200
PFOS in #14155	THF/MeOH or THF/chlorobenzene	%M/M	3	0.0701	0.0181

Table 3: observed differences between THF extraction and other extractions

From table 3 it is clear that the choice of extraction solvent may have a significant effect on the PFOA/PFOS content found. The size of the effect is obviously dependent on the sample type. In the case of sample #14154 the effect is much stronger than in the case of sample #14155.

A minority of the participants used cryogenic milling to reduce the grain size of the sample. About the same number of participants did not reduce the grain size at all, but used the samples as received. The rest of the participants used other methods to reduce the initial grain size to either <1 mm or <0.5 mm or <0.2 mm, see the details in appendix 2.

The test results of the laboratories that used cryogenic milling to reduce the sample to fine powder were significantly higher than the test results of the participants that did not use this sample preparation step, and close to the added amounts of 0.06%M/M, see table 4. Therefore it was decided to use assigned values based on a sub set of test results determined after cryogenic milling of the samples.

	Sample size reduction	unit	n	average	st.dev.
PFOS in #14154	None, used as received	%M/M	12	0.0002	0.0002
PFOS in #14154	Power after cryogenic milling	%M/M	13	0.0015	0.0009
PFOS in #14155	None, used as received	%M/M	13	0.0434	0.0220
PFOS in #14155	Power after cryogenic milling	%M/M	13	0.0467	0.0126

Table 4: observed differences between effect of cryogenic milling against original grain size

From table 4 it is clear that the grain size reduction step may have a significant effect on the PFOA/PFOS content found. The size of the effect is obviously dependent on the sample type. In the case of sample #14154 the effect is much stronger than in the case of sample #14155.

5   CONCLUSIONS

The average value of all reported test results of 0.0009%M/M PFOS for sample #14154, is extremely small. The added amount of PFOS is 0.06%M/M, which means that only 1.5% may have been recovered on average. When only results from cryogenic milling were used, the average value is 0.0015%M/M, which is a recovery of only 2.5%. The theoretical concentration of 0.06%M/M, calculated from the addition of PFOS during the preparation of the samples, was confirmed before use of the sample in the PT, by oxygen combustion and determination of total fluoride.

The final assigned value for PFOS in sample #14155 is 0.047%M/M. The theoretical value, derived from the PFOA amount used during the preparation is 0.06%M/M, which means that 78% may have been recovered on average, which may be just acceptable.

It is unknown what causes the large difference in extraction characteristics and thus in the recovery percentage between sample #14154 and #14155.

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.
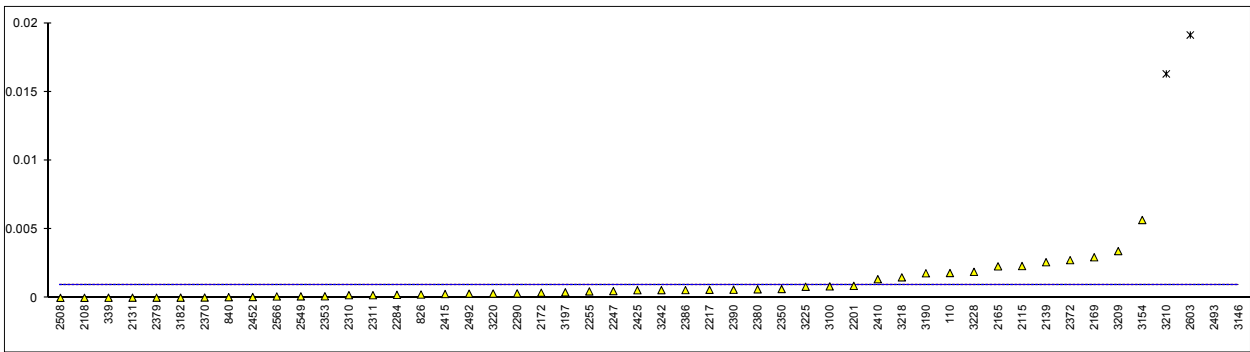
APPENDIX 1

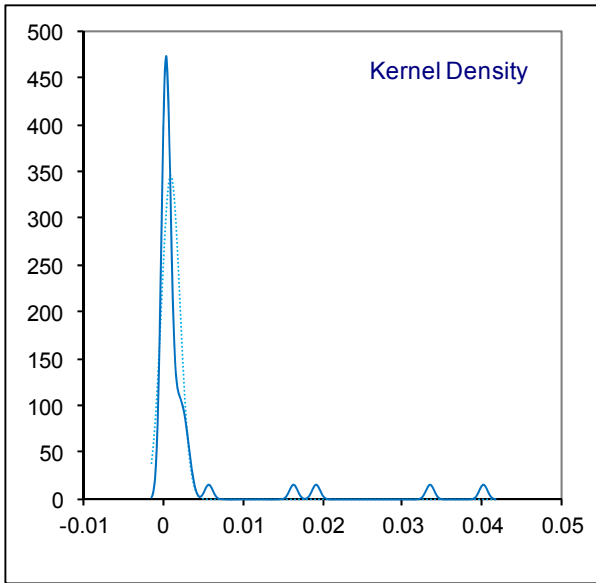Determination of PFOA on sample #14154; results in %M/M

lab	method	value	mark	z'(targ)	remarks
110	INH-291	n.d.		-----	
339	in house	<0.0000050		-----	
622		-----		-----	
826	INH-219	0		-----	
840	in house	n.d.		-----	
2108	in house	n.d.		-----	
2115	in house	n.d		-----	
2131		-----		-----	
2139	CEN/TS15968	<0.001		-----	
2165	in house	<0.0001		-----	
2169	in house	<0.0005		-----	
2172	in house	<0.0001		-----	
2201	CEN/TS15968	<0.0001		-----	
2217	in house	0.00011		-----	
2247	CEN/TS15968	<0.000001		-----	
2255	in house	n.d.		-----	
2284	EPA3550/EPA8321	<0.00001		-----	
2290	CEN/TS15968	<0.0001		-----	
2310	in house	n.d.		-----	
2311	CEN/TS15968	n.d.		-----	
2350	in house	<0.0001		-----	
2353	in house	n.d.		-----	
2370	INH-219	n.d.		-----	
2372	EPA3540C	n.d.		-----	
2375	INH-122	n.d.		-----	
2379	in house	n.d		-----	
2380	in house	n.d.		-----	
2386	in house	<0.000002		-----	
2390	in house	n.d.		-----	
2410	in house	<0.0000001		-----	
2413		-----		-----	
2415	in house	n.d.		-----	
2425	in house	n.d.		-----	
2452	CEN/TS15968	n.d.		-----	
2492	in house	n.d.		-----	
2493	in house	0		-----	
2508	DIN38407	n.d.		-----	
2549	in house	n.d.		-----	
2566	in house	n.d.		-----	
2603		-----		-----	
3100	CEN/TS15968	n.d.		-----	
3146	in house	<0.0001		-----	
3154		-----		-----	
3163		-----		-----	
3172	CEN/TS15968	<0.001		-----	
3176	in house	n.d.		-----	
3182	CEN/TS15968	n.d.		-----	
3190	CEN/TS15968	n.d.		-----	
3197	CEN/TS15968	n.d.		-----	
3209	in house	<0.001		-----	
3210	CEN/TS15968	n.d.		-----	
3218	in house	<0.0001		-----	
3220	in house	0.0145		-----	
3225	in house	0.0000007		-----	
3228	in house	n.d.		-----	
3237		-----		-----	
3242	in house	n.d.		-----	
	normality	unknown			
	n	20			and 29 other laboratories reported 'n.d.'
	outliers	0			
	mean (n)	<0.001			
	st.dev. (n)	n.a.			
	R(calc.)	n.a.			
	R(lit.)	n.a.			

Determination of PFOS on sample #14154; results in %M/M

lab	method	value	mark	z'(targ)	remarks
110	INH-291	0.0018144		-----	
339	in house	0.0000181		-----	
622		-----		-----	
826	INH-219	0.00025		-----	
840	in house	0.0000577		-----	
2108	in house	0.00001071		-----	
2115	in house	0.00232		-----	
2131	in house	0.00002		-----	
2139	CEN/TS15968	0.0026		-----	reported also 0.042 mg/kg and 0.041 mg/kg (other solvents)
2165	in house	0.0023		-----	
2169	in house	0.00296		-----	
2172	in house	0.000383		-----	
2201	CEN/TS15968	0.00088		-----	
2217	in house	0.00059		-----	
2247	CEN/TS15968	0.0005		-----	
2255	in house	0.000477		-----	
2284	EPA3550/EPA8321	0.000225		-----	reported 2.25 mg/kg
2290	CEN/TS15968	0.0003305		-----	
2310	in house	0.0002		-----	
2311	CEN/TS15968	0.0002		-----	
2350	in house	0.00065		-----	
2353	in house	0.000123		-----	
2370	INH-219	0.0000329		-----	
2372	EPA3540C	0.00275		-----	
2375	INH-122	n.d.		-----	
2379	in house	0.00002		-----	
2380	in house	0.000629		-----	
2386	in house	0.0005716		-----	
2390	in house	0.00060		-----	
2410	in house	0.0013631		-----	
2413		-----		-----	
2415	in house	0.000282		-----	
2425	in house	0.000564		-----	
2452	CEN/TS15968	0.000070583		-----	
2492	in house	0.00031163		-----	
2493	in house	0.03342	R(0.01)	-----	
2508	DIN38407	0.0000092915		-----	
2549	in house	0.000116		-----	reported 1.16 mg/kg
2566	in house	0.00011		-----	
2603	in house	0.01912923736	R(0.01)	-----	reported 191.2923736 mg/kg
3100	CEN/TS15968	0.00084	C	-----	reported 8.4 %M/M
3146	in house	0.0401	R(0.01)	-----	
3154	CEN/TS15968	0.00567		-----	
3163		-----		-----	
3172	CEN/TS15968	<0.001		-----	
3176	in house	n.d.		-----	
3182	CEN/TS15968	0.000024		-----	
3190	CEN/TS15968	0.001796		-----	
3197	CEN/TS15968	0.000414		-----	
3209	in house	0.00341		-----	
3210	CEN/TS15968	0.0163	R(0.01)	-----	
3218	in house	0.0015		-----	
3220	in house	0.00032		-----	
3225	in house	0.000814		-----	
3228	in house	0.0019		-----	
3237		-----		-----	
3242	in house	0.00057		-----	

|		Only 'cryogenic'	Only 'as received'	All results
normality		OK	suspect	not OK
n		13	12	46
outliers		1	1	4
mean (n)		0.00152	0.00022	0.00090
st.dev. (n)		0.000945	0.000245	0.001157
R(calc.)		0.00265	0.00069	0.00324
R(Horwitz')		(0.00102)	(0.00026)	(0.00066)
Recovery		2.5%	0.4%	1.5%

all test results

all test results

Determination of PFOA on sample #14155; results in %M/M

lab	method	value	mark	z'(targ)	remarks
110	INH-291	n.d.		-----	
339	in house	<0.0000050		-----	
622		-----		-----	
826	INH-219	0.00006		-----	
840	in house	0.0000591		-----	
2108	in house	0.00000570		-----	
2115	in house	n.d.		-----	
2131		-----		-----	
2139	CEN/TS15968	<0.001		-----	
2165	in house	<0.0001		-----	
2169	in house	0.00004		-----	
2172	in house	<0.0001		-----	
2201	CEN/TS15968	<0.0001		-----	
2217	in house	0.00155	R(0.01)	-----	
2247	CEN/TS15968	0.000033		-----	
2255	in house	n.d.		-----	
2284	EPA3550/EPA8321	0.0000174		-----	reported 0.174 mg/kg
2290	CEN/TS15968	<0.0001		-----	
2310	in house	0.00003		-----	
2311	CEN/TS15968	n.d.		-----	
2350	in house	0.00025		-----	
2353	in house	0.000038		-----	
2370	INH-219	0.0000151		-----	
2372	EPA3540C	n.d.		-----	
2375	INH-122	n.d.		-----	
2379	in house	n.d.		-----	
2380	in house	0.000018		-----	
2386	in house	0.0000198		-----	
2390	in house	n.d.		-----	
2410	in house	0.0000031		-----	
2413		-----		-----	
2415	in house	n.d.		-----	
2425	in house	n.d.		-----	
2452	CEN/TS15968	0.000009685		-----	
2492	in house	0.00000499		-----	
2493	in house	0		-----	
2508	DIN38407	0.0000082426		-----	
2549	in house	n.d.		-----	
2566	in house	0.0000018		-----	
2603		-----		-----	
3100	CEN/TS15968	n.d.		-----	
3146	in house	<0.0001		-----	
3154	CEN/TS15968	0.00036	R(0.01)	-----	
3163		-----		-----	
3172	CEN/TS15968	<0.001		-----	
3176	in house	n.d.		-----	
3182	CEN/TS15968	0.000131		-----	
3190	CEN/TS15968	n.d.		-----	
3197	CEN/TS15968	0.000028		-----	
3209	in house	<0.001		-----	
3210	CEN/TS15968	0.00018		-----	
3218	in house	<0.0001		-----	
3220	in house	n.d.		-----	
3225	in house	0.0000151		-----	
3228	in house	n.d.		-----	
3237		-----		-----	
3242	in house	n.d.		-----	
	normality	not OK			
	n	22			and 17 other laboratories reported 'n.d.'
	outliers	2			
	mean (n)	0.000044			
	st.dev. (n)	0.00006338			
	R(calc.)	0.000177			
	R(Horwitz')	(0.000052)			
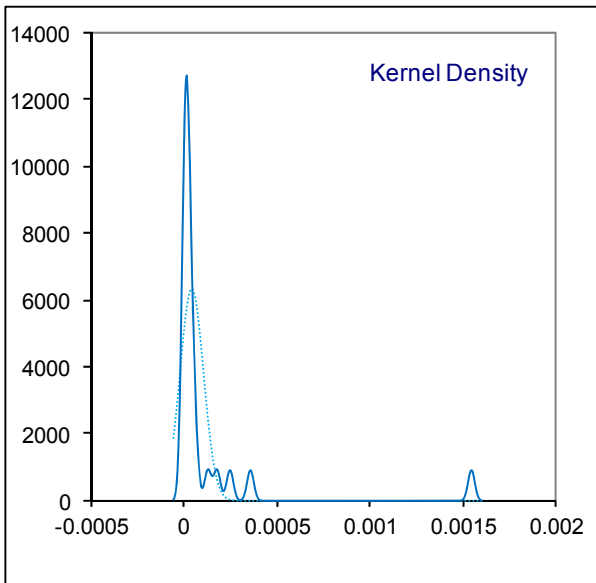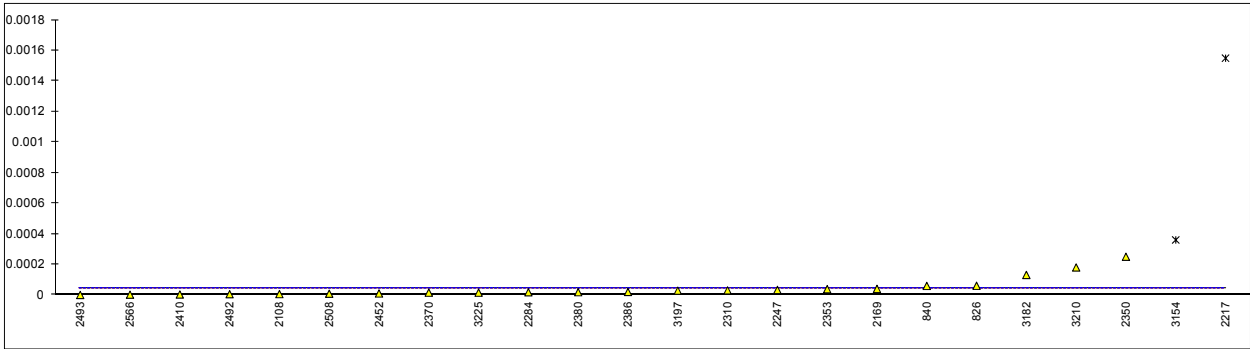
Determination of PFOS on sample #14155; results in %M/M

lab	method	value	mark	z'(targ)	remarks
110	INH-291	0.059702		2.45	
339	in house	0.0083900		-7.25	
622		-----		-----	
826	INH-219	0.05994		2.50	
840	in house	0.06084		2.67	
2108	in house	0.00779361		-7.36	
2115	in house	0.04513		-0.30	
2131	in house	0.002205		-8.42	
2139	CEN/TS15968	0.061		2.70	
2165	in house	0.0477		0.18	
2169	in house	0.05467		1.50	
2172	in house	0.0326		-2.67	
2201	CEN/TS15968	0.04527		-0.28	
2217	in house	0.00713		-7.49	
2247	CEN/TS15968	0.025400		-4.03	
2255	in house	0.036		-2.03	
2284	EPA3550/EPA8321	0.0253		-4.05	reported 253 mg/kg
2290	CEN/TS15968	0.0286459		-3.42	
2310	in house	0.0433		-0.65	
2311	CEN/TS15968	0.046		-0.14	
2350	in house	0.07		4.40	
2353	in house	0.0571		1.96	
2370	INH-219	0.0450		-0.33	
2372	EPA3540C	0.0525		1.09	
2375	INH-122	0.04245		-0.81	
2379	in house	0.018		-5.43	
2380	in house	0.049612		0.54	
2386	in house	0.03301		-2.59	
2390	in house	0.05949		2.41	
2410	in house	0.0530101		1.19	
2413		-----		-----	
2415	in house	0.068		4.02	
2425	in house	0.0639		3.25	
2452	CEN/TS15968	0.014634		-6.07	
2492	in house	0.00833200		-7.26	
2493	in house	0.42584	R(0.01)	71.68	
2508	DIN38407	0.221	R(0.01)	32.95	
2549	in house	0.05986		2.48	
2566	in house	0.00608		-7.69	
2603	in house	0.064270632		3.32	reported 642.70632 mg/kg
3100	CEN/TS15968	0.04413	C	-0.49	reported 441.3 %M/M
3146	in house	0.0584		2.21	
3154	CEN/TS15968	0.01754		-5.52	
3163		-----		-----	
3172	CEN/TS15968	0.0172835		-5.57	
3176	in house	0.00752		-7.41	
3182	CEN/TS15968	0.0095953		-7.02	
3190	CEN/TS15968	0.046387		-0.06	
3197	CEN/TS15968	0.02502		-4.10	
3209	in house	0.05238		1.07	
3210	CEN/TS15968	0.0909		8.35	
3218	in house	0.046		-0.14	
3220	in house	0.0199		-5.07	
3225	in house	0.0314		-2.90	
3228	in house	0.0495		0.52	
3237		-----		-----	
3242	in house	0.0611		2.72	

			Only 'cryogenic'	Only 'as received'	All results
normality	OK		OK	OK	OK
n	13		13	13	51
outliers	0		0	1	2
mean (n)	0.04673		0.04673	0.04337	0.03999
st.dev. (n)			0.012642	0.022032	0.021126
R(calc.)			0.03540	0.06169	0.05915
R(Horwitz')	0.01481		0.01481	0.02276	0.01265
Recovery			78%	72%	67%
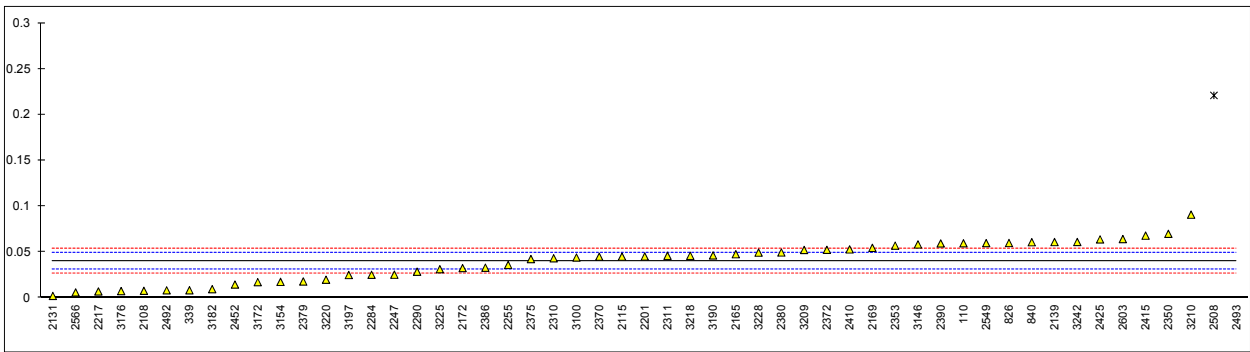
all test results
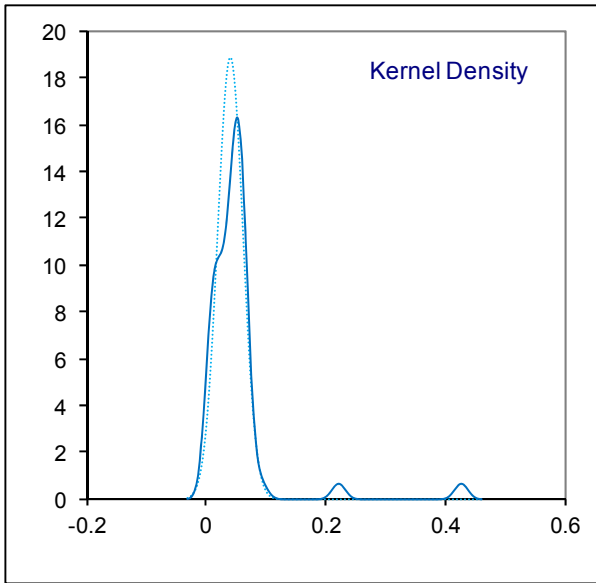
all test results
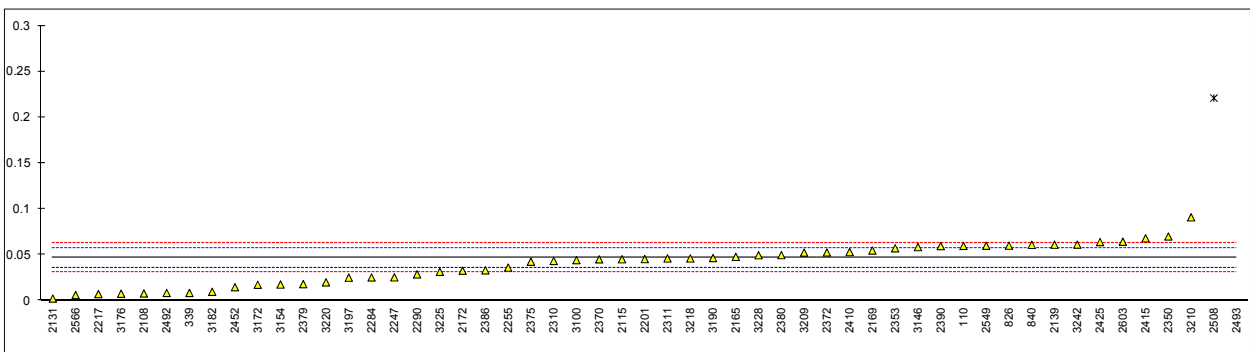
Mean based on cryogenic milling test results only

APPENDIX 2

Analytical details

lab	sample cryogenic milled?	reduced to maximum particle size	Particle size checked	Solvent(s) used	Recovery checked	Internal std used
110	No	<3 mm	Visual	DCM/MeOH	Not checked	Not used
339	No	As received		MeOH	Yes, 85-87%	^{13}C-PFAO, ^{13}C-PFOS
622						
826	No			DCM/MeOH	Yes, 92-95%	
840	No	3 x 3 mm		DCM/MeOH	Yes, 99-101%	
2108	No			MeOH	Not checked	^{13}C-MPFOS, ^{13}C-MPFOA
2115	No			DCM/MeOH	Not checked	^{13}C-MPFOS
2131				MeOH	Not checked	MPFOS, MPFOA
2139	Yes			MeOH, THF/MeOH, DCM/MeOH	Not checked	
2165	Yes	<500 µm	0.5 mm sieve	MeOH	Not checked	Not used
2169	Yes	<250 µm	Visual	MeOH	Not checked	Not used
2172	No	1 x 1 mm	Not checked	MeOH	Yes, 97-98%	Not used
2201	Yes	<500 µm	0.5 mm sieve	MeOH	Not checked	Not used
2217	No	<1 mm		MeOH	Yes, 83-84%	
2247	Yes	<500 µm	Visual	MeOH	Yes, 90%	^{13}C-PFAO, ^{13}C-PFOS
2255	No	cut as small as possible		Methanol	Yes	Not used
2284	No	As received	Not checked	MeOH	Yes, 99%	Not used
2290	No	< 1 mm		MeOH	Yes, 95-96%	^{13}C-PFAO, ^{13}C-PFOS
2310	No	5 mm	graph paper	DCM/MeOH	Not checked	Not used
2311	No	< 3 mm	graph paper	DCM/MeOH	Not checked	
2350	No	3 x 3 mm		DCM/MeOH	Yes, 90%	Not used
2353	No	3 x 3 mm	ruler	DCM/MeOH	Not checked	N/A
2370	No	As received		DCM/MeOH	Yes, 90-95%	N/A
2372	Yes	<500 µm	Visual	MeOH	Yes, 102%	Not used
2375	No	2.5 x 2.5 mm	Vernier Caliper		Yes, 85%	
2379	No	> 1 mm		DCM/MeOH	Yes, 100%	Not used
2380	No	As received		DCM/MeOH	Yes, 96%	Not used
2386	Yes	<500 µm		MeOH	Not checked	^{13}C-PFAO, ^{13}C-PFOS
2390	No	< 1 mm	Vernier Caliper	DCM/MeOH	Yes, 122%	Not used
2410	Yes	<200 µm	0.2 mm sieve	MeOH	Yes, 82.9-119%	Not used
2413	No			Acetonitrile	Yes, 105%	N/A
2415	Yes	<500 µm		MeOH	Yes, 83%	Not used
2425	No	As received		MeOH	Yes, 90.6%	Not used
2452	No	As received	4 mm sieve	MeOH	Not checked	^{13}C-MPFOS, ^{13}C-MPFOA
2492	No			MeOH	Not checked	MPFOS, MPFOA
2493	Yes	<500 µm		DCM/MeOH	Not checked	
2508	No	As received	Not checked	MeOH	Not checked	MPFOS, MPFOA
2549	No	As received		DCM/MeOH	Not checked	
2566	No			MeOH	Yes, 100%	Not used
2603	No	< 1 mm		THF/MeOH	Not checked	
3100	No	<500 µm	0.5 mm sieve	MeOH	Not checked	Not used
3146	No	As received		Chlorobenzene/THF	Not checked	^{13}C-PFOS
3154	No			Acetone	Yes, 47-105%	^{13}C-MPFOA
3163						
3172	No			MeOH	Not checked	
3176	No	As received		MeOH	Not checked	Dr. Ehrenstorfer
3182	No			MeOH	Not checked	
3190	Yes	<125 µm	0.125 mm sieve	MeOH	Yes, 111%	^{13}C-PFOS
3197	Yes	<500 µm	0.5 mm sieve	MeOH	Not checked	MPFOS
3209	No	< 2 mm	2 mm sieve	DCM/MeOH	Yes, 92%	Not used
3210	No			THF/MeOH ultrasonic	Not checked	
3218	Yes	<500 µm	0.5 mm sieve	MeOH	Not checked	
3220	No	2 mm		MeOH	Not checked	
3225	No	< 1 mm		MeOH	Yes	
3228	Yes	<500 µm	0.5 mm sieve	MeOH	Not checked	
3237				MeOH	Not checked	
3242	No	> 1 mm		DCM/ MeOH	Not checked	

APPENDIX 3

Number of participating laboratories per country

  3 labs in BANGLADESH

  2 labs in FRANCE

  5 labs in GERMANY

  3 labs in HONG KONG

  2 labs in HUNGARY

  7 labs in INDIA

  1 lab in INDONESIA

  2 labs in ITALY

  1 lab in JAPAN

  4 labs in KOREA

10 labs in P.R. of CHINA

  1 lab in PAKISTAN

  1 lab in SWITZERLAND

  2 labs in TAIWAN R.O.C.

  2 labs in THAILAND

  1 lab in THE NETHERLANDS

  1 lab in TUNISIA

  4 labs in TURKEY

  2 labs in U.S.A.

  3 labs in VIETNAM

APPENDIX 4

Abbreviations:

C	= final result after checking of first reported suspect 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
n.a.	= not applicable
n.d.	= not detected

Literature:

1   iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, January 2010

2   Analysis of the risks arising from the industrial use of Perfuorooctanoic acid (PFOA) and Ammonium Perfluorooctanoate (APFO) and from their use in consumer articles. Evaluation of the risk reduction measures for potential restrictions on the manufacture, placing on the market and use of PFOA and APFO, RPS (2010)

3   ASTM E178-02

4   ASTM E1301-03

5   ISO 5725-86

6   ISO 5725, parts 1-6, 1994

7   M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)

8   W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)

9   IP 367/96

10   DIN 38402 T41/42

11   P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)

12   J.N. Miller, Analyst, 118, 455, (1993)

13   Analytical Methods Committee Technical Brief, No4 January 2001

14   The Royal Society of Chemistry 2002, Analyst 2002, 127 page1359-1364, P.J. Lowthian and M. Thompson. (see http://www.rsc.org/suppdata/an/b2/b205600n/)

15   Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), pp. 165-172, (1983)